MAY 10 1927

VOLUME [illegible] SECOND SERIES NUMBER 5

THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED BY

THE

AMERICAN PHYSICAL SOCIETY

BOARD OF EDITORS

Managing Editor: [illegible], University of Minnesota, Minneapolis
K. K. Darrow, E. C. [illegible], W. L. Michels, J. A. Gray, G. R. M. Jauncey,
J. H. Van Vleck, [illegible] Jr., P. W. Bridgman, L. W. McKeehan

MAY, 1927

X-ray Measurements of Copper Single Crystals in Different Directions Relative to the Cathode Stream. Warren W. Nicholas 659
[illegible] Paul Kirkpatrick 685
[illegible] Factor in X-ray [illegible] [illegible] in Diatomic Molecules. IV. Hund's Theory: [illegible] and Band Spectra. Relative Nitrogen and Oxygen Intensity Alternating Intensities. Robert S. Mulliken 627
[illegible] O. Laporte 649
[illegible] Constants from Optical [illegible] the First Long Period. R. C. Gibbs and H. E. White 685
[illegible] Three Electron [illegible] [illegible] Spectra of Ge, Sn, Pb, [illegible] and Cs by Double Vacuum Spectra. Arthur W. Smith and Morgan Murray 699
[illegible] Excitation of [illegible] [illegible] John G. Frayne and Charles W. Jarvis 675
[illegible] Radiation and Polarization. [illegible] Radiation in Diatomic Gases. Walter A. MacNair 677
[illegible] Collisions of [illegible] [illegible] Gases. Gaylord P. Harnwell 688
[illegible] Photo-Electric [illegible] [illegible] Henry E. Dunn 693
[illegible] [illegible] E. P. Hammond 703
[illegible] [illegible] E. O. Hulburt 705
[illegible] [illegible] S. Bowen and M. F. Gaviola 717
[illegible] [illegible] [illegible] J. H. Van Vleck 727
[illegible] [illegible] 746
PROCEEDINGS OF THE AMERICAN PHYSICAL SOCIETY
[illegible] Meeting of Section: Abstracts 1-31—Author Index 748
[illegible] Meeting, March

PUBLISHED BY THE AMERICAN PHYSICAL SOCIETY
[illegible], 1927.

Second Series *May, 1927* *Vol. 29, No. 5*

THE

PHYSICAL REVIEW

X-RAY ISOCHROMATS OF COPPER TAKEN IN DIFFERENT DIRECTIONS RELATIVE TO THE CATHODE STREAM

By Warren W. Nicholas

Abstract

Variation with potential of the intensity of monochromatic x-rays of wavelengths 0.823 to 0.247A for directions making angles of 36°, 90° and 144° with the cathode stream.—X-ray isochromats of copper were taken in three different directions relative to the cathode stream, for a target face making an angle of 25° with the cathode stream. Corrections were made for stray radiation in the neighborhood of the measured beam, for radiation due to secondary hits of cathode electrons which had been reflected backward from the focal spot at large angles, and for absorption in the target. It is established that, within experimental error, an isochromat of frequency ν varies linearly with the potential from potentials about $(5/4)\ H\nu$ to $2H\nu$, where $H\nu$ is the quantum voltage for excitation of frequency ν. The linear portions of the graphs were extrapolated to find the intercept on the intensity axis at $H\nu$. This intercept depended on $H\nu$, and also on θ, the angle between the measured x-rays and the cathode stream. For $\theta=90°$ the intercepts varied between $0.062\ I'$ (for $H\nu=50$ kv.) and $0.085\ I'$ (for $H\nu=15$ kv.) with an average of $0.072\ I'$; for $\theta=36°$ the respective values were $0.076\ I'$, $0.096\ I'$, $0.086\ I'$; for $\theta=144°$, $-0.035\ I'$, $0.010\ I'$, $-0.017\ I'$. I' is the intensity of the isochromat at $2H\nu$. Values of $H\nu$ used were 15, 20, 30, 40, 50 kv. The intercept decreased, in general, for increasing $H\nu$, but for $\theta=36°$ and $\theta=90°$ the change was within the experimental error of $\pm 0.01\ I'$.

Energy distribution in the x-ray continuous spectrum from a thick target.—Kulenkampff's formula for the energy distribution in the x-ray continuous spectrum for $\theta=90°$ does not hold in detail for the higher voltages and different target face inclination used in the present work. Assuming total energy in the continuous spectrum proportional to the square of the voltage on the tube, and assuming suitable modifications of this law, for the forward and backward angles, from Sommerfeld's space distribution of energy as a function of cathode ray velocity, it is shown that the spectrum for the forward angle contains relatively more high frequency rays than the spectrum at 90°, and the spectrum at the backward angle contains relatively more low frequency rays.

Energy distribution in the x-ray continuous spectrum from a thin target.—On similar assumptions as to total energy, the spectra which would have been obtained from a very thin foil of copper are derived from the isochromats by Webster's method. The thin target spectra on a frequency scale, for $\theta=90°$, are horizontal except for a sharp rise in intensity as ν approaches ν_0, the high frequency limit. For $\theta=36°$ the energy is approximately directly proportional to ν except for the region near ν_0, where there is again the sharp increase. For $\theta=144°$ the energy is approximately inversely proportional to ν except near ν_0 where there is a decrease for high voltages.

Theories by Kramers and Wentzel for $\theta=90°$ are in fair agreement with the experiments as to thick target spectra, but if certain assumptions made in this paper are correct, Kramers' predicted thin target spectra are much more nearly in accord with the facts than are Wentzel's.

I. Introduction

PREVIOUS work on x-ray radiation in different directions relative to the cathode stream consists either of measurements of total intensity or of comparisons of the ionization spectrum at forward and backward angles. Inasmuch as a reduction of ionization spectrum measurements to energy spectra is very difficult with our present knowledge, such measurements should be supplemented by others in which these reductions do not occur.

To eliminate these reductions, one may use the isochromat method (measuring ionization at a given wave-length as a function of voltage applied to the tube, for constant current). Since ionization is directly proportional to energy, for a given frequency, and since no errors are involved for which suitable correction cannot be made, the isochromat is of the same form as though energy were directly measured. Although a family of isochromats does not determine the energy distribution in the spectrum without some additional knowledge (such as total energy in the spectrum as a function of voltage), nevertheless the isochromats themselves will often distinguish between a correct and an incorrect theory, and are a very valuable guide in the formulation of a new theory.

II. Apparatus

The x-ray tube was of the Coolidge type, water cooled. The copper target face was inclined at an angle of 25° to the direction of the beam of cathode rays (see Fig. 1). Two parallel iron wires extended from the top of the anode approximately in a plane perpendicular to the cathode stream and in such a position that the cathode stream went between them. This was to prevent deflection of the cathode ray electrons by the electrostatic field near the target.

The anode was outgassed by cathode ray bombardment during evacuation. Toward the end of the outgassing process, small brilliant spots kept flashing up at the focal spot, and these flashes seemed to be simultaneous with abrupt gas discharges which were occurring at the same time. When the isochromats were being taken, an area of about a square millimeter at the focal spot was extremely bright for high currents. Unfortunately the surface of the target was roughened in the process of outgassing, so that not much value can be attached to the penetration measurements.

The focal spot was about seven millimeters broad, and this made necessary some special precautions about the position of the tube. The tube was provided with a lateral adjustment reading to a tenth of a millimeter, and the total radiation from the focal spot was plotted by moving the tube across narrow slits lined with the crystal table axis. The centroid of this graph was then found, and the tube set so that this centroid was lined with the slits. The position of the centroid shifted slightly with voltage and current, but any error in wave-length due either to the initial setting (re-adjusted for each isochromat) or to shift, or to both, must have been less than one x-unit. For an isochromat, the slit near the tube was widened so that the only slit limiting the beam was the one near the crystal. This is important on

account of the variation of the focal spot with voltage and current. Special tests were made to assure that the wires attached to the anode did not limit the beam. To insure definite conditions with regard to polarization, the cathode stream was kept always in the plane of the slits.

The generating plant, the electrostatic voltmeter, and the milliammeter were the same as described by Webster and Hennings,[1] and the calibrations

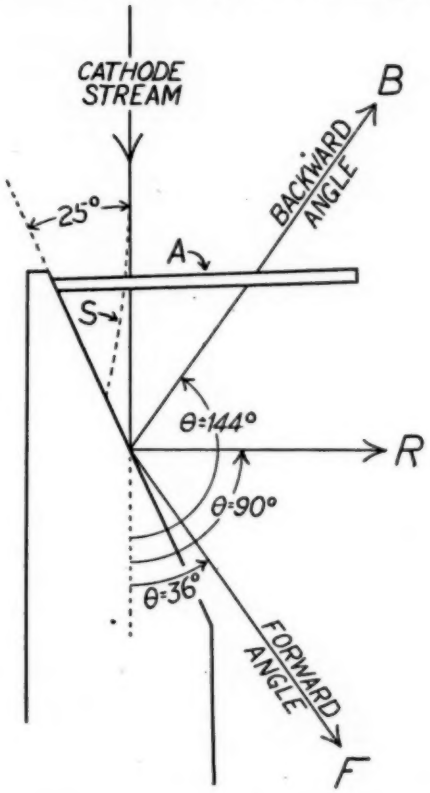

Fig. 1. Schematic diagram of anticathode showing directions of cathode stream and measured x-rays. The cathode stream passed between two wires *A*, which modified the electrostatic field near the anticathode so as to keep the cathode rays from being deflected into some such path as *S*. The continuous x-ray spectra were compared for directions *F*, *R*, and *B*.

and ionization readings were made in the same way. The spectrometer was of the Bragg type, but with a modification[2] which made possible the reading of wave-lengths directly on a micrometer screw. The Compton electrometer was calibrated by an ionization method, keeping the voltage on the tube constant and varying the current.

III. Corrections

The isochromats required corrections of three different types, to be discussed in this section. First, the stray radiation in the neighborhood of the

[1] D. L. Webster and A. E. Hennings, Phys. Rev. **21**, pp. 301–325 (1923).
[2] W. W. Nicholas, J.O.S.A. & R.S.I. **14**, p. 61 (January, 1927).

beam reflected from the crystal was evaluated by plotting it for different positions of the ionization chamber and interpolating to the position for the reflected beam. This radiation was probably due chiefly to diffuse scattering from the crystal.[3] This correction averaged about two percent at the top of the isochromat.

The second correction was for a radiation produced over the whole surface of the target; it is thought to have been due to electrons which had been reflected from the focal spot at large enough backward angles to hit the target face a second time. Curves of the intensity of this radiation at a given wave-length as a function of voltage applied to the tube will be called "secondary isochromats." These secondary isochromats were determined by supporting a piece of lead so as to cut off the radiation from the focal spot and widening the slit nearest the tube in order to measure the radiation from the rest of the target face. They appeared to be linear, from about $(3/2)H\nu$ to $2H\nu$, where $H\nu$[4] is the quantum voltage for production of rays of frequency ν. The extrapolation of the linear portion always gave a negative intensity intercept at $H\nu$. This intercept was always a considerable fraction (1/4 to 2/3) of the intensity of the secondary isochromat at $2H\nu$. At $H\nu$ the secondary isochromats were tangential to the voltage axis. The actual correction was estimated on the assumption that the secondary isochromat radiation was produced uniformly over the target face. The amount of the correction was about three percent at $2H\nu$.

Third is the correction for absorption in the target. The swiftly moving electrons which make up the cathode stream will penetrate into the target, most of them suffering deflections but some of them going in fairly straight lines, and losing energy because of their impacts with the atoms of the target. A few of them will radiate x-rays somewhere along their path, but at any point they cannot radiate a frequency greater than that corresponding to the energy with which they reach the point, according to the Einstein relation. For instance, the maximum frequency of the spectrum must be produced very near the surface of the target, before the electrons have lost appreciable velocity. There will be a maximum depth at which any other frequency may be produced, corresponding to the maximum depth to which a cathode ray can penetrate and still retain enough of its original velocity to be capable of radiating this frequency. But rays of this frequency may be produced at any depth between zero and this maximum, so that in general there will be a depth distribution. The direction in which the absorption of the target for the x-rays is least will be, of course, the direction of the normal to the surface of the target. However, restricting ourselves to directions in the plane perpendicular to the cathode stream, the direction of least absorption will be the direction R (Fig. 1), the absorption increasing as the direction of observation makes greater angles with R, until the angle 90° is reached, when there is infinite absorption.

[3] For a more complete discussion, see the paper by Webster and Hennings, reference 1.

[4] H is equal to h/e, where h is Planck's constant, and e is the charge on the electron, as follows from Einstein's relation $Ve=h\nu$.

Now it is entirely possible that the fully corrected radiation for the direction R differs from that for directions perpendicular to the cathode stream but not in the plane of the paper, because, although there is symmetry about the cathode stream, there is not symmetry about the normal to the target face. For instance, one may easily imagine that the rays are slightly polarized in a direction normal to the face of the target. But as P. A. Ross[5] has recently shown, polarization in the continuous spectrum is appreciable only near the high frequency limit, and errors in this region will affect the present results very little.

Accordingly, the correction for absorption in the target was made on the assumption that the fully corrected isochromats are dependent only on the angle θ (angle between cathode stream and measured x-rays) and independent of the angle ϕ (specifying angular position of the tube about the cathode stream as axis, and measured from the position of least target absorption,

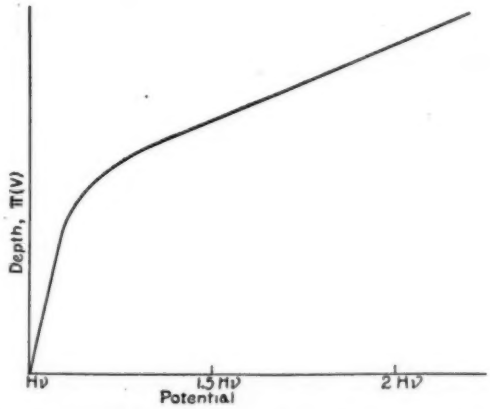

Fig. 2. Relative mean depth of production of rays of frequency ν as a function of voltage on the tube (after Webster and Hennings). $H\nu$ is the excitation potential for frequency ν.

the direction R, Fig. 1). Let $I=f(V)$ represent the fully corrected isochromat of wave-length λ and excitation voltage $H\nu$, for $\theta=90°$. Assume that at a given voltage all the rays of wave-length λ may be considered as having been produced at some definite depth p, measured perpendicular to the face of the target, and let p vary with voltage according to the function $\Pi(V)$ shown in Fig. 2. (The curve of Fig. 2 was obtained by Webster and Hennings[1] for molybdenum at the K absorption limit wave-length and a target face inclination of about 55°. The scale of ordinates is omitted here). For the present target face inclination of 25° the depth measured along the path of the x-rays for $\theta=90°$ and $\phi=0°$ will be $x=p/\cos 25°=1.10p$. If ϕ is increased, this effective depth increases; values of ϕ were actually used corresponding to effective depths x, $2.5x$, and $5x$. The measured isochromats of wave-length λ for effective depth rx should then be represented by

$$I_{rx}=f(V)e^{-\mu rx}=f(V)e^{-1.10\mu r\Pi(V)}$$

[5] P. A. Ross, Phys. Rev. **28**, 425 (1926), abstract.

where e is the base of natural logarithms, and μ is the absorption coefficient of copper for wave-length λ. If each ordinate is then divided by the ordinate in the same isochromat at $V = V_1$, the ratio, which will be called I'_{rx}, should be given by

$$I'_{rx} = \frac{f(V)}{f(V_1)} e^{1.10\mu r[\Pi(V_1)-\Pi(V)]}$$

The purpose of this last step is to reduce different isochromats to comparable scales. V_1 was chosen at about two-thirds of the way up the isochromat, where the relative intensity was considered most certain both on account of having a fairly large value and on account of the possibility of comparing it with points on either side.

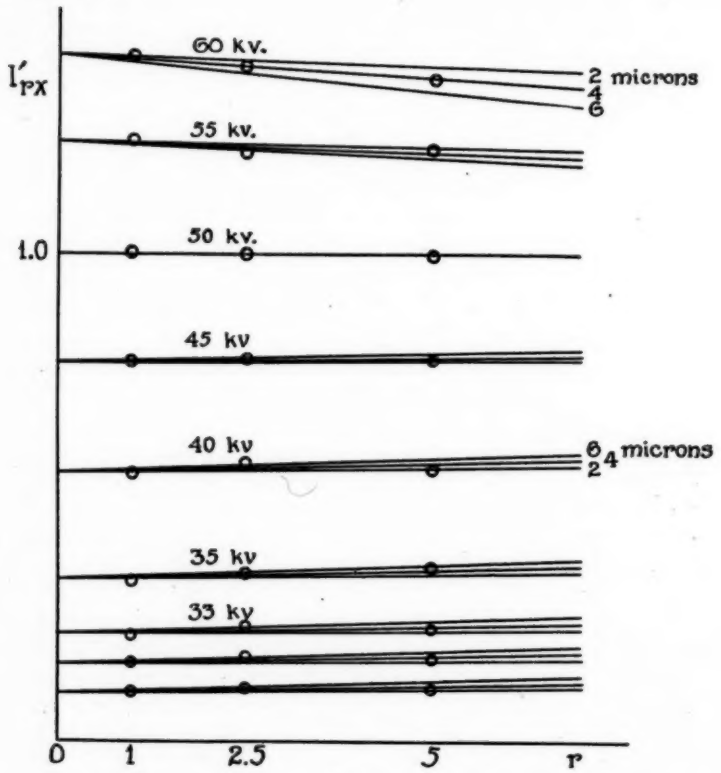

Fig. 3. Illustrating method for determination of the mean depth of production of x-rays in the anticathode.

Experimental values of I'_{rx} can be obtained directly from the data, and their dependence on r may then be compared with this expression as in Fig. 3 (the circles indicate experimental values). According to the formula the points corresponding to a definite voltage ought to lie on an exponential curve. Now the experimental results (compare Fig. 3) show that the slope of the curve must be very small in the vicinity of $r = 1$ to 5; this indicates that in reality the coefficient by which r is multiplied in the exponent is very small.

Accordingly, in the region to be considered, the curvature of the exponential line must be inappreciable. This accounts for the fact that the results of Fig. 3 seem to be fairly well represented by straight lines. Therefore the values for $r=0$ (corresponding to no target absorption) were obtained by extrapolating by means of straight graphs. The deviations from the predicted linearity, which were almost always of the kind shown in Fig. 3 (indicating too much absorption for $r=2.5$), are probably due chiefly to the roughness of the target face.

The graphs of I'_{rz} against r for the 30 kv isochromats are shown in Fig. 3. The families of lines correspond to mean depths of production at 60 kv of 2.0, 4.0, and 6.0 microns respectively. Similar families of lines were drawn for each set of isochromats. The depths selected, however, were not those which best fit the curves for that particular isochromat, but rather which lined up best with the curve of depths at $2H\nu$ for all the isochromats. The curve which was finally selected is shown in Fig. 4. In this connection it is worth noting

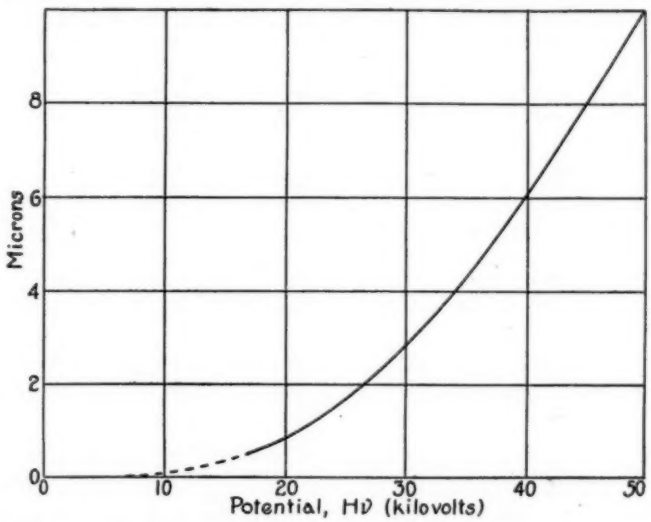

Fig. 4. Mean depth of production of rays of frequency ν at $2H\nu$.

that the values of r used in the corrections were nearly 1 for the backward angle and 5 for the forward angle. For this reason the values of I'_{rz} for $r=2.5$ were given very little weight in the selection of the mean depths for $2H\nu$. From Figs. 2 and 4 all the later absorption corrections could be made on the assumption that p is independent of the direction of observation of the x-rays. Absorption coefficients were calculated from a formula given by Richtmyer.[6]

IV. Results

In Figs. 5, 6, and 7 are shown the fully corrected isochromats for $\theta=90°$, $\theta=36°$, and $\theta=144°$, reduced to the same intensity at $2H\nu$. The forward angle, 36°, and the backward angle, 144°, were selected supplementary so as

[6] F. K. Richtmyer, Phys. Rev. **27**, 1 (1926).

to have polarization the same. For a copper target, the face of which is inclined at 25° to the cathode stream, and for the voltage range here investigated, it seems to be established that:

(1) An isochromat of frequency ν is linear, within experimental error, from about $(5/4)H\nu$ to $2H\nu$, where $H\nu$ is the quantum voltage for excitation of frequency ν.

(2) The linear portions of the graphs were extrapolated to find the intercepts on the intensity axis at $H\nu$. These intercepts, for $\theta=90°$, are within the limits of $+0.073I' \pm 0.02I'$, where I' is the intensity of the isochromat at twice the excitation voltage. The variation of the intercepts with $H\nu$ for $\theta=90°$ is within experimental error.

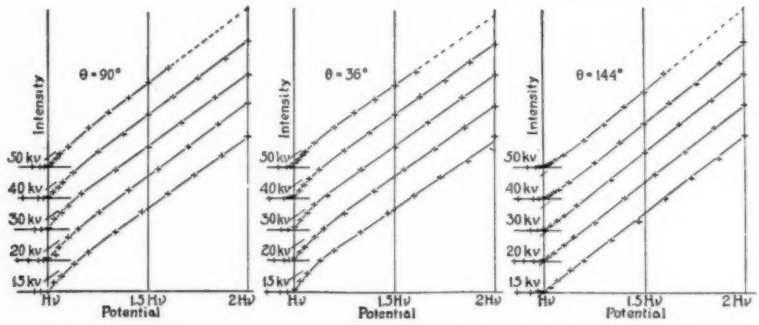

Fig. 5. Isochromats for $\theta=90°$ reduced to equal intensities at $2H\nu$. θ is the angle between cathode stream and measured x-rays.

Fig. 6. Isochromats for $\theta=36°$ reduced to equal intensities at $2H\nu$.

Fig. 7. Isochromats for $\theta=144°$ reduced to equal intensities at $2H\nu$.

(3) The intercepts for $\theta=36°$ were greater than those at 90° by about $0.01I'$, but this amount is not outside the limits of error. These intercepts were likewise independent of $H\nu$.

(4) The intercepts for $\theta=144°$ show a variation with voltage which is outside the experimental error, the intercept decreasing for increasing $H\nu$. The difference between these intercepts and the ones for $\theta=90°$ and $\theta=36°$ is well outside the limits of error, especially at high voltages, where the intercepts for $\theta=144°$ have a *negative* value.

A table of values for the intercept, obtained from the graphs, is shown below. The experimental error is about $\pm 0.01I'$. If anything, the results for $\theta=36°$ are less reliable than the others on account of the larger correction necessary for absorption in the target.

TABLE I

Quantum voltage of isochromat (kilovolts)	Intercepts $\theta=36°$	$\theta=90°$	$\theta=144°$
15	+0.096 I′	+0.085 I′	+0.010 I′
20	+0.093 "	+0.075 "	0 "
30	+0.077 "	+0.072 "	−0.018 "
40	+0.086 "	+0.065 "	−0.040 "
50	+0.076 "	+0.062 "	−0.035 "

V. Discussion

i. Empirical formulas for spectra at 90°. Kulenkampff[7] has proposed the formula[8]

$$I_\nu = C\{Z(\nu_0 - \nu) + Z^2 b\} \tag{1}$$

to express the results of his work on the continuous spectrum at voltages from 7 to 12 kilovolts for an angle of 90° between cathode stream and measured x-rays. I_ν is the intensity on a frequency scale at frequency ν, C is a constant, Z is the atomic number of the metal of the anticathode, ν_0 is the high frequency limit of the spectrum, dependent, of course, on the applied voltage, and b is approximately equal to 0.0025 when ν is measured in units 10^{18} sec^{-1}. This formula would give, for copper, isochromats whose intercepts (see above) are very approximately $0.01\ ZI'/V_0$, where V_0 is the excitation voltage of the isochromat. The present work, and also the work of Webster and Hennings on molybdenum,[1] indicates very definitely that this formula for the intercepts cannot be correct at the higher voltages. On the other hand, the condition that the isochromat intercept shall be nearly constant (as indicated by the isochromat work) is approximated by the formula

$$J_\nu = C\{Z(\nu_0 - \nu) + b'Z^2\nu_0\} \tag{2}$$

Putting $b' = 0.0019$ to give the isochromat intercepts for copper as low a value as allowable ($0.05I'$) from the present experiments, the spectrum intercepts coincide with those of formula (1) for 5400 volts, but are 2.2 too big at 12,000 volts.

It may be that some more general formula is required which will approximate (1) at low voltages and (2) at high voltages, but it is perhaps more likely that several dissimilarities in experimental conditions are responsible for the disagreement. For instance, in Kulenkampff's experiments the cathode stream was perpendicular to the crystal table axis, while in the present work the two were parallel. The former arrangement would cause a loss of intensity due to the reflection of polarized rays from the crystal, but since the spectrum is strongly polarized only near the high frequency limit,[5] the factor should be negligible. A more promising source of explanation is the following extension of an idea of Kramers[9] to explain the discrepancy between his theory and Kulenkampff's experiments. Kramers' theory predicted that the second term on the right hand side of formula (1) should be zero, and Kramers offered the suggestion that since many of the electrons of the cathode stream suffer large deflections on entering the target, some will be deflected out of the target with fairly high speed and in such a manner that they do not return to the focal spot and therefore are lost, in so far as concerns the radiation

[7] H. Kulenkampff, Ann. der Physik, **69**, 548 (1922).

[8] A formula based on Webster's formula for isochromats (Phys. Rev. **9**, p. 220, 1917) would represent much more closely the actual shape of the spectra near the high frequency limit, but for the present discussion of the magnitude of the intercepts, Kulenkampff's simpler formula is adequate.

[9] H. A. Kramers, Phil. Mag. **46**, 869 (1923).

actually measured. The form of the secondary isochromats of the present work suggests that the explanation may be well founded. These deflections vary with the atomic number of the metal of the anticathode, and it would be surprizing if the number and speeds of the electrons lost did not depend on the angle between target face and cathode stream (90° in Kulenkampff's experiments; 25° here).[10] More detailed discussion of the point must, however, await further experiment.

ii. Thick target spectra in different directions. As noted above, a family of isochromats does not determine the energy distribution in the spectrum without some additional knowledge, such as total energy in the spectrum as a function of voltage. It is very likely that this total energy will not be the same function of voltage for forward angles as it is for backward angles, and still different for 90°. As a basis for an approximation to these laws, the usually accepted law that the total energy is proportional to the square of the voltage[11] was assumed for 90°, and modifications for forward and backward angles were estimated from Sommerfeld's curves[12] of spatial distribution of energy as a function of cathode ray velocity. The estimated modifications of the V^2 law were: Total energy $= aV^3$ for $\theta = 36°$, and total energy $= bV^{1.3}$ for $\theta = 144°$, where θ is the angle between cathode stream and measured x-rays, and a and b are constants.[13]

For an approximation to the spectrum energy distribution from a thick target, it will be assumed that the isochromats are linear, with zero intensity intercept at V_0, i.e. that they can be represented by the formula

$$I(V, \nu) = k(\nu)(V - V_0)$$

where $I(V, \nu)$ is the energy at frequency ν in a range $d\nu$, for applied voltage V, and V_0 is the quantum voltage for frequency ν. If $k(\nu)$ can be represented by $c\nu^n$, where c is a constant, the exponent n can be readily found by use of the total energy law

$$\int_{\nu=0}^{\nu=\nu_0} I(V, \nu)d\nu = AV^{2+\epsilon}$$

where A is a constant. It turns out, following Webster's analysis,[14] that $\epsilon = n$, and the equation becomes

$$I(V, \nu) = c\nu^{\epsilon}(V - V_0)$$

Thus when $\epsilon = 0$ (spectrum at 90°, see above) the spectra on a frequency scale are represented by straight lines passing through the high frequency limit, and the lines for different voltages are parallel. When ϵ is equal to 1.0,

[10] It is partly for this reason that the correction equivalent to the present secondary isochromat correction cannot be readily estimated for Kulenkampff's work.

[11] See Siegbahn, Spektroskopie der Rontgenstrahlen, p. 201.

[12] See Sommerfeld, Atombau und Spektrallinien, 4th Ed. p. 37.

[13] It should be emphasized that there is no direct experimental evidence for these assumptions in their present form. But the general form of Sommerfeld's space distribution of energy for steady voltages has been confirmed by Loebe (Ann. d. Phys. **44**, 1033, 1914) and others.

[14] D. L. Webster, Proc. Nat. Acad. **5**, 163 (1919).

corresponding to the forward angle of the present work, the spectra are curved concave downward, and have relatively more energy in the high frequencies than the straight line distribution has. For ϵ equal to -0.7 the spectra are curved concave upward, and have relatively more energy in the low frequencies.[15] A consideration of the fact that actually the isochromat intercepts are greater, algebraically, for forward than for backward angles, leads to even greater asymmetry in the spectra.

iii. Thin target spectra in different directions. The difference in the isochromats for the various directions is perhaps most strikingly brought out by a consideration of the spectra that would have been obtained from an exceedingly thin foil of copper. A method for obtaining thin target spectra, involving the Thomson-Whiddington penetration law, and the total energy law, together with isochromat data has been given by Webster and Hennings.[1]

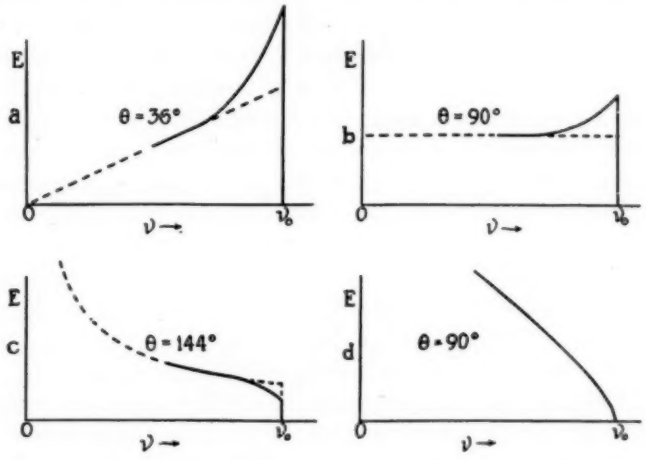

Fig. 8. Energy distribution in thin target spectra. E is the energy on arbitrary scales, θ is the angle between the cathode stream and measured x-rays, ν_0 is the high frequency limit. Curves a, b, c were derived from the isochromats and an assumed total intensity law for the various directions. Curve d is predicted by Wentzel's theory. Curve b, dotted portion, is predicted by Kramers' theory.

From this analysis the energy distribution in the thin target spectrum is given by

$$(b/2V_0)D_V I(V, \nu)$$

where the only quantity not previously defined is b, the coefficient of the Thomson-Whiddington law in the form $V_s^2 = V^2 - bs$. For the simplified case of linear isochromats, this may be written

$$(b/2V_0)k(\nu)D_V(V-V_0) = (c/2V_0)k(\nu)$$

where c is a constant. Taking the formerly determined values for $k(\nu)$, it is obvious that the thin target spectra on arbitrary intensity scales are of the forms indicated by the dotted lines in Fig. 8. If, now, account is taken of the

[15] Compare Wagner's spectra in different directions J. d. Rad. Elek. **16**, 212 (Dec. 1919).

marked deviation from linearity of the isochromats in the region near the quantum voltage, the thin target spectra are modified as shown approximately by the full lines of Fig. 8, a, b, c.

iv. Comparison with theories for spectra at 90°. A theory of the x-ray continuous spectrum proposed by Wentzel[16] predicted that for $\theta=90°$ the spectrum from a thin target should resemble approximately the graph (d) of Fig. 8. Wentzel assumed that the quantum spectrum can be derived from the classical spectrum (emitted by an electron describing a hyperbolic orbit about the nucleus) by a continuous compression of the classical spectrum energy toward lower frequencies, an infinite frequency in the classical spectrum corresponding to the high frequency limit of the quantum spectrum. This is analogous to the method of deriving the quantum line spectrum (e.g. Balmer's series) from the classical spectrum from an electron in an elliptical orbit (fundamental frequency with harmonics). A theory proposed by Kramers[9] proceeded differently, Kramers' method of treatment being simply to chop off the classical spectrum at the high frequency limit given by the Einstein relation, and assume that the frequencies higher than this limit correspond to transitions to stationary states (which practically do not occur). His thin target spectra resembled the dotted portion of Fig. 8*b*. Both theories agree fairly well with experimental results on thick target spectra in spite of the striking disagreement for thin target spectra. This is due to wholly different methods of treating the loss of velocity of the cathode rays on penetrating the target. Kramers assumed that practically all the electrons are slowed up gradually within the target according to the Thomson-Whiddington law. (The efficiency of production of x-rays is so low that comparatively very few electrons will suffer any sudden losses of energy by radiation). Wentzel, on the other hand, followed Lenard in assuming that a large part of the electrons suffer absorption before they have penetrated far enough to have lost much velocity according to the Thomson-Whiddington law.

It is of very great theoretical importance to determine which of these two fundamentally different forms of the Correspondence Principle is more nearly correct. Now the present thin target spectra were derived from the isochromats on the assumption that practically all of the electrons are slowed up gradually within the target (i.e. that Lenard's absorptions are inappreciable). But on the other hand, if Lenard's absorptions had been assumed to be of chief importance, the derived thin target spectra at 90° would have resembled Wentzel's. Evidently then, one cannot, on the basis of the present work, discriminate between the two theories without a knowledge of what actually happens to the cathode rays on entering the target.

Kulenhampff[17] has recently discussed these absorptions for the passage through air of electrons having an initial velocity corresponding to voltages in the neighborhood of 10 kv. This was in connection with experimental work on the total ionization in air produced by photoelectrons which had been

[16] Gregor Wentzel, Zeits. f. Physik, **27**, 257 (1924).

[17] H. Kulenkampff, Ann. der Physik, **80**. 3. p. 261, June 2, 1926.

ejected by x-rays of known energy. It appears that for these conditions Lenard's absorptions are extremely rare. If it could be concluded from this that the absorptions are also negligible in the present work, then the continuous compression theory of Wentzel could be said quite definitely to be wrong. It is scarcely permissible, however, to carry over the results for low voltages and gaseous media to high voltages and solid media.[18] Nevertheless, it is difficult to understand what becomes of the energy of the electron in these atomic absorptions, considering the conservation of energy and the conservation of momentum together with the fact that the probability of production of an x-ray is extremely small.

v. Comparison with theories for spectra in different directions. As to the isochromats in the different directions relative to the cathode stream, neither Kramers' nor Wentzel's theory is developed to such an extent as to allow ready comparison of experiment with theory. It may be pointed out simply that the present results are in qualitative agreement with what would be expected if these theories were modified in some such way as that developed by Sommerfeld (see above) to account, by means of classical electrodynamics, for the early work in this field. It should be strongly emphasized that although considerations such as are elaborated in the first part of this discussion make it difficult to interpret theoretically the absolute magnitude of the intercepts of the present work, the difference between the intercepts for various angles between cathode stream and measured x-rays is not to be explained in this manner.

This work was done at Stanford University. I wish to thank Professor D. L. Webster, under whose guidance the work was completed, for his very generous help and advice. This paper has been revised and extended since the author became a National Research Fellow at Cornell University; I am grateful for having had the opportunity to discuss the paper with Professor H. A. Lorentz and Professor F. K. Richtmyer.

CORNELL UNIVERSITY,
December 14, 1926.

[18] See also two papers by P. Lenard, Ann. d. Physik, **80**, pp. 1–32 (May 18, 1926).

THE POLARIZATION FACTOR IN X-RAY REFLECTION

By Paul Kirkpatrick

Abstract

The polarization factor for the reflection of polarized x-ray radiation. An x-ray beam consisting of a multiplicity of superposed polarized radiations with non-coincident planes of polarization will exhibit the same scattering distribution in a plane normal to the beam as will a beam consisting of two plane polarized components, suitably intense, whose planes of polarization are mutually perpendicular. The customary polarization factor $\frac{1}{2}(1+\cos^2 2\theta)$ does not apply to reflection of polarized radiation and should be replaced by

$$\frac{\sin^2\alpha+P\cos^2\alpha+(P\sin^2\alpha+\cos^2\alpha)\cos^2 2\theta}{1+P}$$

In this quantity P is the primary polarization ratio and α is an angle defining the orientation of the tube with respect to the plane of reflection. For the orientation most often employed the new polarization factor reduces to $(P+\cos^2 2\theta)/(1+P)$. Radiation from a tube so oriented that α is 45° will be reflected with the same intensity as an equally intense unpolarized radiation, the polarization factor assuming the familiar form $\frac{1}{2}(1+\cos^2 2\theta)$. This orientation is recommended for future investigations, since it necessitates no knowledge of the primary polarization. A *new method for measuring the polarization of homogeneous x-rays* is presented.

Introduction

THE so-called polarization factor which appears in formulas expressing the intensity of x-rays reflected from crystals was first developed by Sir J. J. Thomson,[1] and serves to account for the decrease of intensity which the change in direction incurs. The factor expresses the proportional reduction of intensity involved in this process, and is written $\frac{1}{2}(1+\cos^2 2\theta)$. The factor may also be written $(\frac{1}{2}+\frac{1}{2}\cos^2 2\theta)$, thus exhibiting the fact that the intensity of the deviated portion of one-half of the incident (unpolarized) radiation is constant with the angle of deviation, while the intensity of the deviated portion of the other half varies as $\cos^2 2\theta$. The electric vectorial components of that half of the incident radiation which gives rise to the constant deviated portion lie in a direction at right angles to the plane of reflection while the components of the half which gives rise to the variable portion lie in the plane of reflection.

Although the polarization factor was designed to apply only to an unpolarized incident beam, those who have made use of it have not always been mindful of this limitation. Indeed the writer has not been able to discover a single case in the literature of crystal reflection where this restriction has been recognized, though the polarization factor has entered into the numerical computations of numerous papers.[2] The continuous spectral

[1] Thomson, Conduction of Electricity Through Gases.

[2] A. H. Compton, Phys. Rev. **7**, 658 (1916); Bragg, James, and Bosanquet, Phil. Mag. **41**, 308 (1921), and later papers; Harris, Bates, and MacInnes, Phys. Rev. **28**, 235 (1926). These papers are representative of a much larger number which might be cited.

radiation from primary x-ray sources is never unpolarized, and Bishop's[3] results indicate that the characteristic radiations may not be assumed to be free from polarization either. It is desirable to develop a polarization factor which shall apply to reflection of x-radiation initially partially or completely polarized.

An Equivalence Theorem

As a preliminary step it will be well to simplify our method of representing the beam emitted from the x-ray tube. The beam as actually emitted is complex, and must be supposed to be constituted of a large number of elementary emissions having their planes of polarization oriented in many different directions. It will now be shown that this beam scatters identically with a much simpler beam, consisting of two components polarized in mutually perpendicular planes. It is well known that the predominant direction

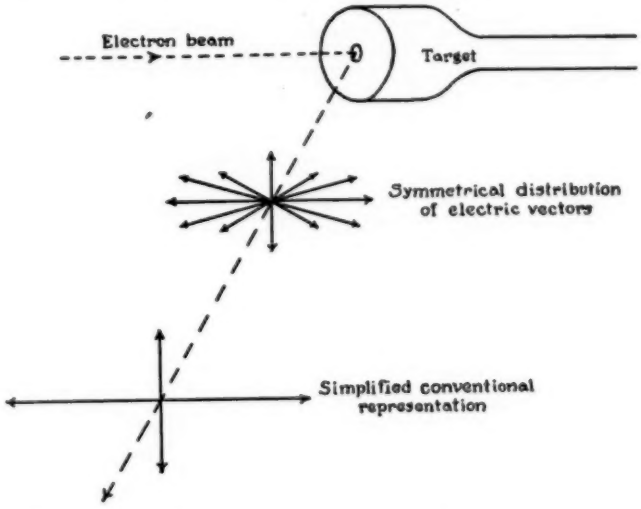

Fig. 1. Complex x-ray beam made up of a multiplicity of independent emissions. The electric vectors of the separate emissions are symmetrically disposed with respect to their prevailing direction, and in the present consideration may be replaced by two mutually perpendicular vectors.

of the electric vectors of the real beam lies in a plane containing the cathode stream. The symmetrical scattering of the beam on either side of this direction shows furthermore that the distribution of the planes of polarization of all the wave trains is a statistically symmetrical one with respect to the favored direction. The state of affairs is conventionally depicted in Fig. 1, where for every electric vector of amplitude E and inclination δ to the predominant direction there is represented also a similar electric vector symmetrically inclined upon the other side of the predominant direction. Fig. 1 also shows an equivalent system of two mutually perpendicular vectors, which will be shown to be a permissible substitution.

[3] Bishop, Phys. Rev. **28**, 625 (1926).

When such a beam is incident upon a scattering body of low atomic number the intensity of radiation scattered in any direction perpendicular to the beam is proportional to the sum of the squares of the amplitude components perpendicular to that direction. If the intensities of radiation thus scattered in the directions of minimum and of maximum scattering be compared experimentally, as has frequently been done, a ratio is obtained which characterizes the state of polarization of the beam as a whole, and which may be expressed

$$P=\frac{\sum(E\sin\delta)^2}{\sum(E\cos\delta)^2} \tag{1}$$

Eq. (1) may also be stated in two other forms which will presently be found useful. They are

$$\Sigma(E^2\cos^2\delta)=\Sigma E^2/(P+1) \quad \text{and} \quad \Sigma(E^2\sin^2\delta)=\Sigma E^2/(1+1/P) \tag{2}$$

Consider now the intensities of radiation scattered in two other mutually perpendicular directions, also normal to the direction of propagation of the beam. One of these directions of scattering, A, makes an angle ϵ with the

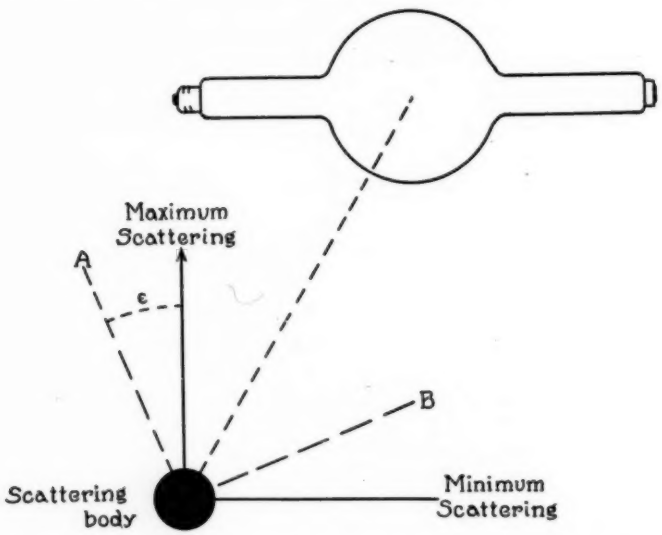

Fig. 2. X-ray scattering in a plane normal to the direction of propagation.

direction of maximum scattering. The ratio of the intensity of radiation thus scattered in the direction of B to that scattered in the direction of A, Fig. 2, may be formulated thus.

$$R=\frac{\sum(E\sin[\delta-\epsilon])^2+\sum(E\sin[\delta+\epsilon])^2}{\sum(E\cos[\delta-\epsilon])^2+\sum(E\cos[\delta+\epsilon])^2} \tag{3}$$

The double summations in numerator and denominator are necessary to take care of both members of the symmetrical pairs of electric vectors.

Upon expansion and simplification of Eq. (3) there is obtained

$$R=\frac{\cos^2\epsilon\sum E^2\sin^2\delta+\sin^2\epsilon\sum E^2\cos^2\delta}{\cos^2\epsilon\sum E^2\cos^2\delta+\sin^2\epsilon\sum E^2\sin^2\delta} \tag{4}$$

Substituting from Eq. (2) this becomes

$$R=\frac{P\cos^2\epsilon+\sin^2\epsilon}{\cos^2\epsilon+P\sin^2\epsilon} \tag{5}$$

It is apparent from this result that R is a function simply of P and ϵ, and does not require any special distribution of the individual δ's. It is therefore permissible as far as R is concerned to assume any desired distribution for the planes of the elementary emissions. The simplest and most convenient assumption is that the emitted beam is made up of two plane polarized components with their electric vectors mutually perpendicular, the direction of one of them being parallel to the cathode stream. The relative amplitudes of these components may be chosen so as to give any value of P which a complex real beam might possess. Since the real beam may be replaced by the duplex beam without affecting R it may be concluded that any real beam will exhibit the same scattering distribution in a plane normal to the beam as will a beam consisting of two plane polarized components, suitably intense, whose planes of polarization are mutually perpendicular.

Generalization of the Polarization Factor

In the beam of x-rays incident upon the reflecting crystal we need consider only such portion as is of the proper wave-length for reflection at the existing grazing angle, θ. Let this portion be regarded as consisting of two superposed plane polarized beams of the kind just discussed. The amplitudes may be designated by L and T, the greater one being L. The magnitudes of these amplitudes are governed by the requirements that $T^2+L^2=$ total intensity, and $(T/L)^2=P$.

For simple visualization let it be supposed that the plane of reflection is horizontal and that the x-ray tube is capable of rotation about the incident beam as axis. The orientation of the tube at any time may be specified by the angle α, between the plane of reflection and a plane defined by the incident beam and the cathode stream. Resolving the amplitudes T and L horizontally and vertically we have as vertical components $L\sin\alpha$ and $T\cos\alpha$, and as horizontal components $T\sin\alpha$ and $L\cos\alpha$. The reflected intensity due to the vertical components is constant with the angle of deviation, so that the intensity of this reflection portion is proportional to $(L\sin\alpha)^2+(T\cos\alpha).^2$ The reflected intensity due to the horizontal components varies as $\cos^2 2\theta$, so that the intensity of this portion is proportional to $[(T\sin\alpha)^2+(L\cos\alpha)^2]\cos^2 2\theta$. We therefore have

$$\text{Polarization factor}=\frac{\sin^2\alpha+P\cos^2\alpha+(P\sin^2\alpha+\cos^2\alpha)\cos^2 2\theta}{1+P} \tag{6}$$

Discussion

When the incident radiation is unpolarized P has the value unity, and Eq. (6) assumes the familiar form $\frac{1}{2}(1+\cos^2 2\theta)$. The tube orientation most often employed is probably that defined by $\alpha=0$. Investigators seldom if ever state the values of α employed in their work, but the diagrams accompanying all of the papers cited in footnote 2, indicate that the zero value was used in these cases. For this orientation we have

$$\text{Polarization factor } (\alpha=0)=(P+\cos^2 2\theta)/(1+P)$$

Uncertainty as to the correct values of P makes it impossible to apply exact corrections to work done in the past. A computation based upon values regarded as plausible has shown however that some of the numerical results given in the papers cited should be modified by as much as ten percent.

Lacking precise information as to the values of P it is by all means desirable that future investigations involving comparisons between theoretical and observed intensities of reflection should be carried out with the x-ray tube oriented so that $\alpha=45°$, that is, with the plane determined by the cathode stream and the incident ray inclined at an angle of 45° with the plane of reflection. In this case the right member of Eq. (6) becomes $\frac{1}{2}(1+\cos^2 2\theta)$, and P need not be known. Radiation received from a tube thus inclined will be reflected with the same intensity as unpolarized radiation, regardless of what its actual state of polarization may be.

The determination of P for x-rays of different wave-length and different conditions of exictation has been attempted by the writer[4] and by Ross,[5] using methods in which the intensity of radiation scattered by non-crystalline solids was measured. The results contained in the present paper furnish us with a simple and apparently superior method for the determination of this quantity. Let x-rays be reflected from a crystal with the x-ray tube in the $\alpha=0$ position, and again with the tube in the $\alpha=90°$ position. Measure the intensities of reflection by an ionization method and call their ratio K. Then K is the ratio of the polarization factors for the two positions, and it follows quite simply that for the wave-length reflected

$$P=\frac{K-\cos^2 2\theta}{1-K\cos^2 2\theta}$$

Determinations by this method are now in preparation.

Department of Physics,
University of Hawaii,
Honolulu, T.H.,
February 10, 1927.

[4] Kirkpatrick, Phys. Rev. **22**, 226 (1923).
[5] Ross, Bull. Am. Phys. Soc. Vol. 1, No. 10.

ELECTRONIC STATES AND BAND SPECTRUM STRUCTURE IN DIATOMIC MOLECULES. IV. HUND'S THEORY; SECOND POSITIVE NITROGEN AND SWAN BANDS; ALTERNATING INTENSITIES

By Robert S. Mulliken

Abstract

After a brief review of Hund's theory of molecular electronic states and band spectra, and a discussion of intensity relations and selection principles in terms of the correspondence principle, it is shown that practically all the available evidence, as embodied in previous papers of this series and elsewhere, is in agreement with the theory. The occurrence of ρ-type S terms and σ-type P and D terms is explained by the theory, as also the existence of ρ-type and σ-type doubling. Selection rules and other relations in $^2P \rightarrow {}^2S$ and $^2S \rightarrow {}^2P$ transitions (including, in agreement with Mecke and Hulthén, the CH, OH, MgH, and CaH bands) are discussed. Hund's interpretation of the second positive nitrogen bands as a $^3P \rightarrow {}^3P$ transition is further developed, and extended to the Swan bands; the apparent absence of Q branches, and other intensity relations in these bands, are explained; the rotational doubling in these bands (accompanied by alternating intensities) is interpreted as σ-type doubling. It is shown that the alternating intensities or alternate missing lines in the He_2, N_2, Swan, and N_2^+ bands can all be accounted for formally by the postulate that they are due to alternate (partially or completely) suppressed levels such that the suppressed values of $(j_k - \sigma_k)$ are always as follows: B rotational sub-states, $(j - \frac{1}{2} - \sigma_k) = 0, 2, 4, \cdots$; A sub-states, $1, 3, 5, \cdots$; here σ_k is the part of σ which is due to the orbital angular momentum of the electron, and j_k is the resultant of σ_k and the quantity m which measures the nuclear angular momentum in quantum units.—Finally, the questions of term-notation and -formulation, j values for odd and even molecules, etc., are considered. The NH β bands ($^3P \rightarrow {}^3S$) are briefly discussed.

Introduction—Review of Hund's Theory. In a very important paper,[1] Hund has discussed from a theoretical standpoint the question of the nature of molecular electronic states, by a consideration of the orders of magnitude of the various electrical and magnetic interactions to be expected in a system composed of electrons and two nuclei.

Hund assumes that, as in atomic spectra, each electron (in particular, the τ'th electron) has orbital angular momentum corresponding to the (azimuthal) quantum number k, and in addition, a half-quantum ($s = \frac{1}{2}$) of spin angular momentum; the resultant of all the k_τ's is denoted k, and that of the s_τ's is denoted s.

Hund shows that in ordinary cases we may expect k to execute an essentially uniform precession about the internuclear axis, because of the strong axial field which must result (superposed on a central field) from the presence of two nuclei. The corresponding quantum number σ_k represents the component of k along the internuclear axis, and should be subject to the selection rule $\Delta\sigma_k = 0$ or ± 1 (for justification, cf. following section).

[1] F. Hund, Zeits. f. Physik, **36**, 657 (1926). The notation used here is different from Hund's; his l, i, and p correspond to k, σ, and j as used here.

By analogy with atomic spectra, Hund assumes that the electric field of the nuclei has no effect on s, but that s tends to interact magnetically, as in the atomic case, with k. Since k should ordinarily precess rapidly about the internuclear axis, only the component along this axis, namely σ_k, is effective in orienting s. If the interaction between σ_k and s is sufficiently intense (case a), s is quantized with respect to the internuclear axis, about which it precesses; the corresponding quantum number may be designated σ_s. By analogy to the rule $\Delta m_s = 0$ (m = magnetic quantum number) in the Paschen-Back effect in atoms, Hund concludes that σ_s should be subject to the rule $\Delta\sigma_s = 0$. Since $\sigma = \sigma_k + \sigma_s$, it follows from the selection rules for σ_k and for σ_s that the rule $\Delta\sigma = 0$ or ± 1 should hold.

Hund shows that with a given value of σ_k, the various possible orientations of s in case (a) should give rise to a multiple electron level having (usually[2]) the same number of components as for a multiple atomic level possessing values of k and s equal to those of σ_k and s in the present case. Unlike the atomic multiplet, however, the components should all be equally spaced, but the spacing should be of the same order of magnitude as for a similar multiplet in an atom.

If the interaction between s and σ_k is small (case b), the torque which causes s to follow the motion of the internuclear axis may become inadequate as the rate of nuclear rotation increases. A gradual transition should then occur with increasing j, to a condition in which s is oriented and quantized with respect to j_k (j = resultant of j_k and s), j_k being the resultant of m and σ_k (here $\sigma_k = \sigma$). The expected selection rules in the extreme case are $\Delta\sigma_k = 0$ or ± 1, $\Delta j_k = 0, \pm 1$, and $\Delta j = 0, \pm 1$.

Hund also discusses the question of fine structure. For additional details, reference should be made to Hund's paper, and to the excellent discussion by Kemble.[3] In a brief review of the empirical data, Hund presented evidence of good agreement with his theory. One of the main objects of the present paper is to give a more complete discussion of the evidence, including that recently obtained by the writer and given in previous papers of this series and elsewhere.[4,5,6,7]

Selection rules and intensity relations. The question of selection rules and intensity relations has been treated only briefly by Hund. For an understanding of the experimentally observed relations in terms of the theory, and of the connection of the Hönl and London-Dennison intensity equations

[2] Unlike the atomic case, the full number of components corresponding to the multiplicity should always be developed with the P terms; e.g. a ^4P term would have four components ($\sigma_k = 1$, $\sigma_s = \pm\frac{1}{2}, \pm 1\frac{1}{2}$), instead of three as in the atomic case.

[3] E. C. Kemble, Bulletin of National Research Council Subcommittee on Molecular Spectra, pp. 326–331 and 345–6 (1927).

[4] R. S. Mulliken, Proc. Nat. Acad. Sci. **12**, 151 (1926).

[5] R. S. Mulliken, Phys. Rev. **28**, 481 (1926).

[6] R. S. Mulliken, Phys. Rev. **28**, 1202 (1926).

[7] R. S. Mulliken, Phys. Rev. **29**, 391 (1927).

with Hund's molecular model, a somewhat more detailed consideration is needed. This can be given in terms of the correspondence principle.[8]

Let us begin with a particular harmonic component of frequency α,—corresponding to a particular change in the total and azimuthal or other quantum numbers of the electron, and in the nuclear vibrational quantum number,[9]— in the Fourier analysis of the motion of the emitting electron, this harmonic component being taken with reference to a system of axes precessing with the electron orbit about the internuclear axis and of course also following the latter axis in its precession about the axis of total angular momentum. (Strictly, because of the slight perturbation of the orbital motion by the spin s, α should be considered as split into a group of components $\alpha \pm \tau\omega_s$, where ω_s is the frequency of precession of s about the internuclear axis; but, corresponding to the selection rule $\Delta\sigma_s = 0$, the amplitudes of all the components having $\tau > 0$ may be considered negligible). If now we transform to a set of axes fixed in the molecule, one of these being the internuclear or σ axis, the previous harmonic component α yields in general only three components (in so far as the precession of k about σ is uniform) of frequencies α (linear component along σ) and $\alpha \pm \omega_\sigma$ (right- and left-handed circular components about σ). Here ω_σ is the frequency of precession of k about the σ axis, and corresponds to the quantum number σ_k. The three components thus respectively correspond to the transitions $\Delta\sigma_k = 0$ and ± 1. For brevity these three frequencies will be called β^0, β^+, and β^-. The question of the relative amplitudes of these three components need not concern us here.

Now let us consider any one of the above components β, and let us suppose that we are dealing with Hund's case (a). Transforming to a set of axes fixed in space, one axis being in the direction of j, we obtain in general three new components, namely a linear component, of frequency β, along j, corresponding to $\Delta j = 0$ (Q branch), and two circular components, of frequencies $\beta \pm \omega_j$, corresponding to $\Delta j = \pm 1$ (R and P branches); ω_j is the frequency of precession of σ about j. The relative amplitudes of these components can be expressed as trigonometric functions of the angle θ whose cosine is σ/j; this is true even if σ differs from σ_k because of the presence of σ_s. The appropriate functions (cf. ref. 7, Eq. 3; the functions given in Eq. 3 are proportional to radiation intensities) are identical in form with those for $\Delta j = 0, \pm 1$ in a line spectrum multiplet, since the Fourier components corresponding to $\Delta\sigma_k = 0, \pm 1$ are identical in form and type (referred to the σ axis) with those (referred to the k axis) associated with $\Delta k = 0, \pm 1$ in the atomic case; in the latter case $\cos\theta = (j^2 + k^2 - s^2)/2jk$. (We are here neglecting the effect of molecular vibration,—first pointed out by Kemble; for refs. cf. ref. 7. This alters the amplitude factors somewhat, in the molecu-

[8] For a detailed discussion of the methods of the correspondence principle, cf. E. Buchwald, "Das Korrespondenzprinzip," F. Vieweg & Sohn, Braunschweig (1923); J. H. Van Vleck, Nat. Res. Council Bulletin No. 54, "Quantum Principles and Line Spectra," Chapter IX (1926); M. Born, "Atommechanik," especially pp. 118–121 (J. Springer, Berlin, 1925).

[9] Cf. A. Kratzer, Naturwiss. **27**, 577 (1923); W. Lenz, Zeits. f. Physik, **25**, 299 (1924); . Condon, Phys. Rev. **28**, 1182 (1926).

lar case.) The identity just stated formed the starting point of Hönl and London's derivations of their equations. In a previous paper[7] it was stated that Hönl and London's three cases (Eqs. 4, 5, 6 of ref. 7) should correspond primarily to $\Delta\sigma_k=0, \pm1$ rather than to $\Delta\sigma=0, \pm1$; the reasons for this statement will now be evident from the discussion given above.

In Hund's case (b), starting with any one of the three harmonic components β, we first transform to a set of axes, one of which is along j_k, and which precess with j_k about j. This gives three components of frequencies β and $\beta\pm\omega_{jk}$, which for brevity may be denoted γ^0, γ^+, and γ^-, corresponding to transitions $\Delta j_k=0, \pm1$. The relative intensities are then given in the same form as before (Eq. 3 of ref. 7); but here $\cos\theta=\sigma_k/j_k$. The next step, using any one of the components γ, is to transform to axes which are fixed in space and one of which is parallel to j. The precession of j_k and s about their resultant j is completely analogous to the precession of k and s about their resultant j in the line spectrum case. Hence the relative intensities for the three components of frequencies γ, $\gamma\pm\omega_j$, corresponding to $\Delta j=0, \pm1$, are again given by Eq. (3) of ref. 7, if here θ is the angle (usually small) between the vectors j_k and j, and if $\sigma'-\sigma''$ in Eq. (3) is replaced by $j_k'-j_k''$. By examination of Eqs. (3) it can be seen that if $\cos\theta=1$, all the intensities vanish except those for which $\Delta j=\Delta j_k$; while if $\cos\theta$ is very *near* 1, as is necessarily the case in practise, except for small values of j_k or large values of s, the remaining intensities are very small. Except for certain weak series, a rule $\Delta j_s=0$ (where $j_s=j-j_k$) should be obeyed in the case of *doublet* terms, where $j=j_k\pm\frac{1}{2}$.

From the preceding we may conclude that in Hund's case (b) the intensity distributions in P, Q, and R branches (neglecting weak satellite lines where $\Delta j\neq\Delta j_k$) should fall under the same types as in case (a), each type being characteristic of a particular combination of values (initial and final) of σ_k and j_k, in the same way as of the σ and j values in case (a). Exact equations analogous to the Hönl and London equations will be given for case (b) in a subsequent paper. For transition cases between (a) and (b), it is not yet obvious what the intensity relations should be.

Singlet electronic states. The writer has shown that the band spectra of various molecules containing an even number of electrons are naturally classified as corresponding to transitions between singlet electronic states (^1S, ^1P, ^1D, $\cdots$,) with $\rho\sim0$ for all and $\sigma=0, 1, 2, \cdots$. The following types of transitions are known (cf ref. 6, Table II): $^1S\rightarrow{}^1S$, $^1S\rightarrow{}^1P$, $^1P\rightarrow{}^1S$, and $^1D\rightarrow{}^1P$. These indicate a selection rule $\Delta\sigma=0, \pm1$. For the case $\sigma=0$, the rotational states are single, for $\sigma>0$, they are double ("σ-type doubling"),[5,6] the two rotational states having equal a priori probability.[7] All these relations are in agreement with Hund's theory if we identify ^1S, ^1P, and ^1D states in the sense here used with the three cases $\sigma_k=0$, 1, and 2 (all with $\sigma_s=s=0$) in Hund's theory. The selection rules $\Delta\sigma_k=0, \pm1$, $\Delta\sigma_s=0$ are obeyed, and the occurrence of single rotational states for $\sigma=0$ and double rotational states for $\sigma>0$ is also in agreement with Hund's predictions. That σ_k (here equal to σ) is really an electronic quantum number

corresponding in general to a precession about the internuclear axis, is supported by the agreement of observed intensity relations,[7] in bands of the types mentioned, with those predicted on the assumption that σ_k *is* such a quantum number. To be sure, the evidence in the cases cited gives no ground for decision as to whether it is $\Delta\sigma$ or $\Delta\sigma_k$ which governs the intensities. In many transitions[4,6] of the type $^2P_{1,2}\rightarrow{}^2S$ and $^2S\rightarrow{}^2P_{1,2}$, however, we have $\Delta\sigma_k=\pm1$, but $\Delta\sigma=\pm\frac{1}{2}$ or $\pm1\frac{1}{2}$, giving evidence that σ_k, not σ, is the real quantum number.

Doublet electronic states. Band spectra corresponding to transitions between doublet electronic states are now known for a number of molecules containing an odd number of electrons. While in singlet states Hund's cases (*a*) and (*b*) are not distinguishable, since $s=0$, the two cases should in general be distinct in doublet states, if we suppose that the latter are characterized by $s=\frac{1}{2}$.

For ^2S states we then expect $\sigma_k=0$ and $j_k=m$ (Hund's case *b* here becomes identical with his case *d*). Since there is no torque to orient s in the σ direction, it might seem that s could orient itself freely in any direction (or with respect to an external magnetic field). But the observed structure of the ZnH and similar bands of a $^2P\rightarrow{}^2S$ type shows that the usual selection rule $\Delta j=0,\ \pm1$ is observed, and that $\rho=\pm\frac{1}{2}$ for ^2S states; also $\sigma=0$ as expected. The definite orientation of s as ρ in ^2S states is attributed by Kemble[3] to an interaction between s and a small magnetic field, parallel to m, developed by the molecule as a result of its rotation. The slight energy difference (ρ-type doubling[5]) which exists, for a given value of m, between F_1 states ($\rho=+\frac{1}{2}$) and F_2 states ($\rho=-\frac{1}{2}$) is also ascribed by Kemble to this field. The observed existence of just two energy levels for each value of j is in agreement with Hund's theory.

In $^2S\rightarrow{}^2S$ transitions,[5,6,10] the observed transitions ($F_1\rightarrow F_1$ and $F_2\rightarrow F_2$) are apparently limited to those in which ρ does not change sign, *i.e.* in which s does not reverse itself. This limitation $\Delta j_s=0$ is in agreement with the theory (cf above under "selection rules" · · · .) for transitions between doublet states which fall under case (*b*). The theory however predicts the existence of additional weak lines, and in particular accounts for the hitherto unexplained (ref. 5, p. 506) apparent existence (ref. 5, p. 489; ref. 10) of an F_2 state with $j=0$; a more detailed discussion of the relation of theory to experiment for $^2S\rightarrow{}^2S$ bands will be given in a later paper.

For ^2P states, Hund's theory predicts $\sigma_k=1$, with $s=\pm\sigma_s=\frac{1}{2}$ in case (*a*), giving $\sigma=1\frac{1}{2}$ or $\frac{1}{2}$; in case (*b*), $\sigma_k=1$, $s=\frac{1}{2}=\pm j_s$. For many molecules (NO β bands,[11] ZnH and other bands listed under $^2P\rightarrow{}^2S$ and $^2S\rightarrow{}^2P$ in Table II of ref. 6), typical ^2P states approximating case (*a*) actually occur, having a double electron level with $\sigma=\frac{1}{2}$ ($^2P_1$) and $\sigma=1\frac{1}{2}$($^2P_2$).

The existence of combinations $^2S\rightarrow{}^2S$, $^2P_{1,2}\rightarrow{}^2S$, $^2S\rightarrow{}^2P_{1,2}$, and $^2P_1\rightarrow{}^2P_1$ and $^2P_2\rightarrow{}^2P_2$ (cf ref. 11, NO β bands), indicates that the selection rule

[10] E. Hulthén, Phys. Rev. **29**, 97 (1927): CaH bands, $^2P\rightarrow{}^2S$ and $^2S\rightarrow{}^2S$ types.

[11] F. A. Jenkins, H. A. Barton, and R. S. Mulliken, Phys. Rev. **29**, 211*A* (1927), and forthcoming detailed articles; Nature, **119**, 118 (1927).

$\Delta\sigma_k=0, \pm1$ is obeyed, while the complete absence of the combinations $^2P_1\rightarrow{}^2P_2$ and $^2P_2\rightarrow{}^2P_1$ in the NO β bands gives striking evidence in support of Hund's rule $\Delta\sigma_s=0$. The intensity relations[11] in the NO β bands also agree with the theory for case (*a*).

In $^2P\rightarrow{}^2S$ and $^2S\rightarrow{}^2P$ transitions involving case (*a*) ^2P states, neither of the rules $\Delta\sigma_s=0$ and $\Delta j_s=0$ can be observed, since ^2S states always fall under case (*b*). Actually in the ZnH, CdH, and HgH bands,[4] we have $+\sigma_s\rightarrow\pm\rho$ in $^2P_2\rightarrow{}^2S$ and $-\sigma_s\rightarrow\pm\rho$ in $^2P_1\rightarrow{}^2S$, [12] giving altogether four P, four Q, and four R branches.

In addition to the more obvious examples of $^2P\rightarrow{}^2S$ and $^2S\rightarrow{}^2P$ transitions, there are several band spectra (CH, OH, MgH, etc.), briefly considered in previous papers,[5,6] which may now likewise be classified as $^2P\rightarrow{}^2S$ (MgH) and $^2S\rightarrow{}^2P$ (CHλ3900, OH), if one supposes with Mecke[13] that the electronic doublet separation ($^2P_1-{}^2P_2$) shrinks rapidly with increasing j. As Hund has shown, this last feature finds a natural explanation in the transition from case (*a*) to case (*b*) of his theory. In this transition $\pm\sigma_s$ should go over, for normal multiplets, according to Kemble (private communication; cf. ref. 26), into $\mp j_s$, resulting in a decreasing electronic energy separation, and in terms of the Kramers and Pauli formula, giving a variable σ and ρ (cf Eqs. 1 and 2 below).

Kratzer's interpretation of the CH bands, recently advocated in slightly modified form by the writer,[5] involves, for the final state of the molecule, a constant $\sigma(\sigma=1)$ and $\rho(\rho=\pm\frac{1}{2})$. For very large values of j this is obviously in harmony with Hund's case (*b*) as above discussed, for a ^2P state. The excellent agreement of the experimental data with Kratzer's interpretation for *small* as well as large values of j must now probably be considered fortuitous (in agreement with Mecke and Birge, and contrary to earlier contentions of the writer[5]) in view of the strength of Hund's theory.

Hulthén has recently concluded[10] that certain CaH bands should be classified, like the MgH bands, as $^2P\rightarrow{}^2S$. These differ from the HgH type bands in that the $^2P_2$ states combine only with the ^2S states having $\rho=-\frac{1}{2}$, and the $^2P_1$ states only with $\rho=+\frac{1}{2}$, so that there are altogether only two P, two Q, and two R branches. Since in case (*b*) we expect (for normal doublets, $j_s=-\frac{1}{2}$ for $^2P_2$ states and $+\frac{1}{2}$ for $^2P_1$ states, this would indicate that the predicted rule $\Delta j_s=0$ (see above under "selection rules · · ·") is effective here as in $^2S\rightarrow{}^2S$ transitions. The $^2P_1$ and $^2P_2$ states both show Q "combination defects" which may be ascribed to σ-type doubling[14] combined with Q "crossing-over,"[15] just as in $^1P\rightarrow{}^1S$ transitions (cf. ref. 6, p. 1205, Eq. (1a), and Fig. 1). In CHλ3900 there are six branches which follow similar selection rules to the CaH bands. The same is true of the OH

[12] There are of course two rotational sub-states, for each of the cases $+\sigma_s$ and $-\sigma_s$; in each case one of these combines with $+j_s$, the other with $-j_s$ (cf. ref. 6, Eq. 8*A*.)

[13] R. Mecke, Zeits. f. Physik, **36**, 795 (1926).

[14] The σ-type doubling appears to be about equally great, in case (*b*), for $^2P_1$ and $^2P_2$ states, judging by the CH and OH bands; in CH (according to Kratzer's analysis) this doubling can be represented by using a double value of B.

[15] R. Mecke, Phys. Zeit., **26**, 227 (1925).

bands, except that there are additional weak branches (satellite series). In these CH and OH bands, or at least in OH, $j_s = +\frac{1}{2}$ for the $^2P_2$ states and $-\frac{1}{2}$ for $^2P_1$, and the ^2P doublet is inverted (cf. later paper), but the $\Delta j_s = 0$ rule still holds (for the six strong branches). In CHλ4300 there are twelve branches, but, as will be shown in a later paper, these bands are due to a $^2D \rightarrow {}^2P$ transition. A detailed comparative study of structure and intensity relations for the whole group of $^2P \rightarrow {}^2S$ and $^2S \rightarrow {}^2P$ transitions will be given in a later paper.

In agreement with Hund's theory, there are in all known ^2P states four rotational states for each value of j except for $j = 1$. In case (a), this results from σ-type doubling[15a] in each of the electronic states $^2P_1$ and $^2P_2$. In case (b), σ_k gives σ-type doubling,[14] and on this is superposed $\pm s$ doubling; for large values of j, the latter goes over into ρ-type doubling, since then $j_s \sim \rho$; furthermore, the σ-type part of the doubling here shows the same properties (cf. above, CaH, CHλ3900, OH) as for typical σ-type states (e.g. ^1P states).[6]

Triplet electronic states: interpretation of second positive nitrogen and Swan bands. We now come to the question of band spectra due to combinations of triplet electronic states. For a ^3P state, $\sigma_k = 1$, $s = 1$; $^3P_0$, $^3P_1$, and $^3P_2$ correspond in Hund's case (a) to $\sigma_s = -1$, 0, and $+1$, respectively, in case (b) to $j_s = \pm 1$, 0, ∓ 1. Hund gives a theoretical diagram (Fig. 4) for a $^3P \rightarrow {}^3P$ transition, and on p. 671–2 makes it probable that the second positive nitrogen bands[16,17,18] are an example of this type corresponding for low values of j to case (a) and for high values to case (b). The fact that (aside from rotational doubling) only three P and three R branches are known in each band is accounted for by the selection principle $\Delta\sigma_s = 0$, or $\Delta j_k = \Delta j$, limiting the intense transitions to $^3P_0 \rightarrow {}^3P_0$, $^3P_1 \rightarrow {}^3P_1$, and $^3P_2 \rightarrow {}^3P_2$.

For small j values, if case (a) holds, the molecular term values should have the form

$$F = F(n) + F(\sigma) + B(j^2 - \sigma^2) + \cdots \qquad (1)$$

Here $F(n)$ is the vibrational term, and $F(\sigma)$ is the electronic term which according to Hund's theory should have three equally spaced values cor-

[15a] The splitting of the rotational levels into two is apparently much more pronounced in $^2P_1$ than in $^2P_2$ states in case (a), (ZnH, CdH, HgH, NO, refs. 4, 11); in fact the experimental evidence for any rotational splitting at all in $^2P_2$ states here is confined to certain perturbed lines in the HgH bands (cf. ref. 4, bottom p. 156, and refs. there given).

[16] E. Hulthén and G. Johansson, Arkiv f. Mat., Astron. och Fysik, **18**, No. 28 (1924); Zeits. f. Physik, **26**, 308 (1924). The designations $\alpha, \beta, \gamma, a, b, c$, are respectively equivalent to $P_3, P_2, P_1, R_3, R_2, R_1$ in the notation of Lindau and Mecke. When used with numerical subscripts, e.g. a_3, the subscript is the value of the quantum designation m; the following relations hold,[18a] P_1, R_1, branches, $j'' = (m + \frac{1}{2}) + 1$; P_2, R_2 branches, $j'' = (m + \frac{1}{2})$; P_3, R_3, $j'' = (m + \frac{1}{2}) - 1$; thus $(m + \frac{1}{2})$ is the same as j_k'' (for values of j sufficiently large so that j_k has a meaning).

[17] P. Zeit, Zeit. Wiss. Photog. **21**, 1 (1921); R. Mecke and P. Lindau, Phys. Zeits., **25**, 277 (1924); P. Lindau, Zeits. f. Physik, **26**, 343; **30**, 187 (1924). Lindau's m values are the same as Hulthén and Johansson's, for the R branch, but one unit lower for the P branch.

[18] R. Mecke, Zeits. f. Physik, **28**, 261 (1924); Phys. Zeits., **25**, 1 (1924).

responding to $\sigma=0$, 1, and 2. For large j values, where case (b) is approximated, the relation is[1]

$$F=F(n)+F(j,j-j_k)+B(j_k^2-\sigma_k^2)+\cdots. \tag{2}$$

The three values of $F(j, j-j_k)$ should be closer together than those of $F(\sigma)$ in case (a), increasingly so with increasing j (cf. Hund's Fig. 3). The arrangement of the band lines and the relation between the j and j_k values for case (b) are shown in Fig. 1.

Several features will now be considered which have been discussed only very briefly or not at all by Hund. Since N_2 is an even molecule, the j values should (in the writer's numbering) be half-integral. That this is

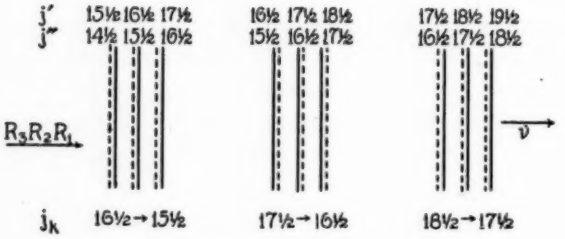

Fig. 1a

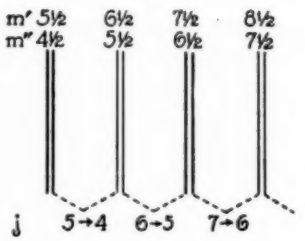

Fig. 1b

Fig. 1a corresponds roughly to the arrangement of the lines (missing lines are dotted) in the R branches of the Swan bands.[18a] The arrangement is similar in the second positive nitrogen bands, except that (1) the dotted components are present but weak, (2) the doublets are unresolved in the R_3 branches and nearly so in R_2 (in regard to the relative positions of the two components in P_2 and R_2 cf. R. Mecke, ref. 16, p. 271, footnote), (3) R_1, R_2, and R_3 are more widely separated for a given value of j_k. The relative position of the strong and weak doublet components in relation to the j values is correct as given, for N_2, but has not been definitely determined for the Swan bands. Fig. 1a is also applicable to the P branches (P_1, P_2, P_3) if the values of j' and j'_k given are reduced by two units.[18a] Fig. 1b shows schematically the arrangement of the strong and weak lines in the R branches in the N_2^+ bands, as given by Fassbender.[22]

true is shown by an examination of the Δ_2F' and Δ_2F'' values for small values of j; these [14,15] are of the expected form $\Delta_2F=4BT$ with approximately half-integral T values, which shows (cf. ref. 5, p. 491) that the j values are half-integral if Eq. (1) is applicable.

The question of missing lines has been discussed by Hund. The theoretical values of j'' for the first line in each branch are readily specified, noting[18a] that $\sigma=0$ for P_3 and R_3, 1 for P_2 and R_2, 2 for P_1 and R_1, and assigning to j_{min} in each case the first half-integral value in excess of σ. In Table I the predicted first lines are compared with those observed. The apparent presence of P_1'' ($2\frac{1}{2}$) is rather disconcerting. The apparent absence of R_1' ($2\frac{1}{2}$) is less strange, since this component of R_1 ($2\frac{1}{2}$) would be weak due to

[18a] It is possible that the assignment of σ values, and the relation of j to j_k, for the P_1R_1 and P_3R_3 branches, should be interchanged in ref. 16, Table I, and Figs. 1a and 2b. Presumably $+\sigma_s$ ($^3P_2$ in case a) goes over into $-j_s$ of case b, and $-\sigma_s$($^3P_0$) into $+j_s$, for normal triplets, and the reverse for inverted triplets. The relation $(m+\frac{1}{2})=j_k''$ of ref. 16 is reliable.

the alternating intensity phenomenon (see below). On the whole the results are not very satisfactory, but the experimental difficulties in determining the presence or absence of weak lines in a crowded region are great.

TABLE I

Values of $j''-\frac{1}{2}$ for first recorded line of each branch

Band	P_1'	P_1''	P_2	P_3	R_1'	R_1''	R_2	R_3
λ3371	3	2	2	1	3	2	2	1
3577	3	2	1	1	3	2	(1)	2
3805	(3)	2	(2)	1	(3)	2	1	0
3536	3	2	(3)	(3)	(3)	(2)	2	1
3755			2	1			(2)	1
3998				1				0
3710			4	1			4	0
3942			4	(1)	3	3	2	(1)
Theory	3	3	2	1	2	2	1	0

Notes. The data for the first five bands are from Hulthén and Johansson,[16] and Zeit.[17]; for the last three, also the presence of $R_3(1)$ in λ3536, the data are according to Lindau.[17] Values in parentheses are uncertain due to superposition.

Closely analogous to the second positive nitrogen bands, as pointed out by Heurlinger, are the Swan (probably C_2 or perhaps C_2H_2) bands,[19,20] which can therefore probably also be classified as $^3P \rightarrow {}^3P$. The triplet separations in these bands are smaller than in the N_2 bands, indicating that Hund's case (*b*) is approached even for rather small j values.

The apparent absence of Q branches in the second positive nitrogen and the Swan bands can be explained by a consideration of the intensity equation of Hönl and London and Dennison for the case $\sigma' = \sigma''$ (cf. ref. 7, Eq. (4)). As in the NO β bands,[11] only very short weak Q branches are to be expected (none at all in the case $^3P_0 \rightarrow {}^3P_0$), whose presence would probably not be noticed without special search.[21,22] Also, corresponding P and R branches should be approximately equal in intensity;[21] so far as can be seen from the available data,[16] this relation is fulfilled. Since according to Hund's theory $^3P_0$, $^3P_1$, and $^3P_2$ states have equal a priori probability for a given value of j, we should furthermore expect $P_1 (= P_1' + P_1''$ in Table I$) = P_2 = P_3 = R_1 (= R_1' + R_2'') = R_2 = R_3$, approximately. This appears to be not in conflict with the data[16,20] (but cf. Lindau, ref. 17, p. 351).

The rotational doubling in the N_2 and Swan bands is presumably σ-type doubling of the type specified by Eq. (2) of ref. 6.[23] In the Swan bands, the doubling is accompanied by alternate missing lines[19] apparently of the same type as in the $^1D \rightarrow {}^1P$ band of He_2 (cf. p. 1208–10 of ref. 6; and cf.

[19] T. Heurlinger, Dissertation Lund, 1918; R. Komp, Zeits. Wiss. Photog., **10**, 123 (1912); etc.

[20] R. Fortrat, Ann. de physique **3**, 350 (1915): Swan band λ5165. R. C. Johnson, Phil. Trans. Roy. Soc. London, **226A**, 157 (1927): comprehensive summary and large amount of new data.

[21] The Hönl and London equations are of course directly applicable only for case (*a*), but may be expected to be at least qualitatively applicable here, especially for low values of j.

[22] Certain additional series in the second positive nitrogen bands have been reported by Konen (cf. Heurlinger, ref. 19, p. 55), but are probably due to impurities (cf. ref. 16).

[23] Mecke earlier interpreted this doubling in the N_2 bands as ρ-type doubling.[18]

Fig. 1*a* of the present paper with Fig. 3 of ref. 6). This is true for all three P branches and all three R branches; also, the magnitude of the doublet separations is nearly the same in all three branches of each kind.

Fig. 1*a* shows how the strong and weak doublet components depend on j and j_k in the Swan bands.[18a] It is without doubt significant that the relative positions of the strong and weak components are the same for all three members of a triplet (P_1, P_2, P_3 or R_1, R_2, R_3), hence are determined by j_k, not by j. For large values of j the P_2 and P_3 (eventually also the P_1) branches draw together (similarly with the R branches), and the scale of the multiplicity due to the three orientations of s becomes finer than that of the σ-type doubling. The tendency seems to be toward a coalescence of P_1, P_2, P_3 and R_1, R_2, R_3 each into a single series of alternate-missing-line *doublets* (of the He_2 $^1D \rightarrow {}^1P$ type) whose spacing and intensities are a function of j_k, and are presumably characteristic of σ_k.

The existence of rotational doubling for all three of the electronic states $^3P_0$, $^3P_1$, and $^3P_2$ (in spite of the fact that,—for low values of j,—σ is zero for $^3P_0$, just as for ^1S, where rotational doubling is absent) is in agreement with Hund's theory, and gives the latter further support.

In the N_2 bands, there is an obvious doubling, accompanied by alternating relative intensities of the two components (P_1' and P_1''; and R_1' and R_2''), only in the P_1 and R_1 branches; here the doublet separation is approximately constant ($\Delta\nu \sim 0.24$),[16,17] suggesting that it is mainly "electronic" in origin (cf. ref. 6, bottom of p. 1206). In the P_2 and R_2 branches, the existence of doubling coupled with alternating intensities is made evident by a displacement of the lines alternately to left and right, together with slight diffuseness in certain lines.[17] In the P_3 and R_3 branches, the lines form a single series without alternating intensities, but by analogy with the Swan bands, there is no doubt a latent doubling as demanded by the theory; the existence of two series, related in intensity like those in the P_1 and R_1 branches, but superposed, would account for the observed apparently uniform non-alternating series, while with a truly single series any alternation would necessarily be evident.

The NH *bands: note added in proof.*—The NH bands recently analyzed by Hulthén and Nakamura (Nature, Feb. 12, 1927) and classed by them[23a] as $^3P \rightarrow {}^1S$ are in all probability $^3P \rightarrow {}^3S$. The strong Q branches show $\Delta\sigma_k \neq 0$. The existence of Q combination defects and of three, rather than six, P (and Q, and R) branches show that an S electronic state is involved. (The $P'Q'R'$ branches evidently belong to a second band, as Hulthén and Nakamura point out). The *final* states in fact show a narrow triplet separation increasing linearly with j, as expected for ^3S (case *b*). The initial states, showing wide triplets getting narrower with increasing j, must then be ^3P.

A generalization concerning alternate suppressed rotational levels. Alternate weakened or suppressed lines in the N_2 and Swan bands, as in the He_2 bands (ref. 6, Fig. 2), are presumably due to a partial or complete suppression of alternate *rotational levels*. In the case of He_2, it has been shown[6] that the

[23a] The classification $^3P \rightarrow {}^1S$ was a misprint for $^3P \rightarrow {}^3S$, the writer has since learned from Dr. Hulthén.

observed relations can be explained in terms of a system of missing levels which is characteristic for each type (^1S, ^1P, or ^1D) of electronic state; the suppression of a level is a function only of j and of σ; or, since $s=0$ and $\sigma=\sigma_k$ here, we may say that it is a function of j_k and σ_k. We may say further that, for each of the two types of rotational sub-states in He_2, the suppressed values of $(j_k-\sigma_k)$ are characteristic and independent of σ_k and of the total quantum number of the excited electron, and are as follows (cf. ref. 6, Fig. 2): B sub-states, $(j_k-\frac{1}{2}-\sigma_k)=0, 2, 4, \cdots$; A sub-states, $1, 3, 5, \cdots$; note that for $\sigma_k=0$, only B sub-states occur.[6]

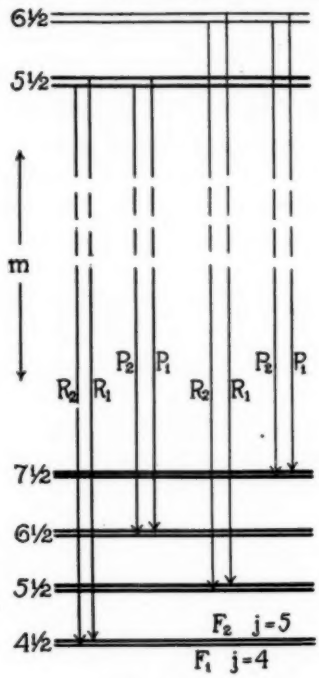

Fig. 2a

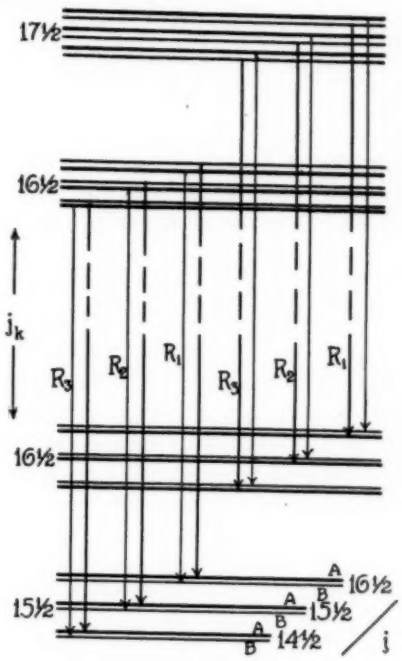

Fig. 2b

Fig. 2. Possible scheme of rotational energy levels and transitions, (*a*) for the negative nitrogen (N_2^+) bands, (*b*) for the Swan and second positive nitrogen bands; in (*b*) the three values of $j(j_k-1, j_k$, and $j_k+1)$ for each value of j_k belong to $^3P_0$, $^3P_1$, and $^3P_2$ levels, respectively.[18a] The spacings and intensities are not to scale. The relative position of the F_1 and F_2 levels in (*a*) and of the A and B levels in (*b*) is not certain; the same is true in (*b*) of the relative magnitude and order of the $^3P_0$, $^3P_1$, and $^3P_2$ levels and of the A and B rotational levels, in initial and final states. In (*b*), if suitable additional rotational levels are used, P branch transitions can be drawn, similar to the R transitions, with no "crossing over"; Q branch transitions should be very weak and involve crossing over ($A\rightarrow B$ and $B\rightarrow A$), according to Eq. (2) of ref. 6.

Since there seems to be no reason why the scheme of alternate partially or wholly suppressed levels as a function of j_k and σ_k should differ from one homopolar molecule to another, it is reasonable to *postulate* that the statement just made for He_2 holds exactly for all homopolar molecules. The data on the N_2 and Swan bands are evidently compatible with this postulate, since the missing or weakened lines are a function of j_k (not of j), hence, we may say (σ_k being the same for all three ^3P states), of $(j_k-\sigma_k)$. In the

N_2^+ bands ($^2S \rightarrow {}^2S$ transition) the two branches (P and R) are each composed of alternately strong and weak doublets;[24] here again (Fig. 1b) weakness or strength is determined by j_k, or $j_k - \sigma_k$, not by j.

In the case of He_2, the *absence* of observed combinations, such as $^1P \rightarrow {}^1P$ and $^1S \rightarrow {}^1S$, between like electronic states was attributed[6] to a *complete* suppression of alternate rotational levels in *both initial and final* states. The *occurrence* of the combinations $^3P_0 \rightarrow {}^3P_0$, etc. in the Swan and N_2 bands, and $^2S \rightarrow {}^2S$ in the N_2^+ bands, then indicates that suppression occurs for one only of the two electronic states (Swan bands) or is only partial (N_2 and N_2^+ bands); partial suppression might be present in either or both of the two states.

A possible arrangement of the rotational levels for the N_2 and Swan bands is shown in Fig. 2b, and for the N_2^+ bands in Fig. 2a. In Fig. 2b the three levels corresponding to $^3P_0$, $^3P_1$, and $^3P_2$ are drawn equidistant in accordance with Hund's theory, and in agreement with the observed approximately equal spacing of the triplets formed by $R_1R_2R_3$ or $P_1P_2P_3$. The latter might, however, have arisen from a suitable non-equidistant arrangement of $^3P_0$, $^3P_1$, and $^3P_2$ in initial and final states. It is also uncertain whether the three levels are more widely spaced in the initial or in the final states, and whether in each case $^3P_2$ is the highest level as in a normal multiplet or the lowest as in an inverted multiplet.[18a] The relative magnitude etc. of the rotational doubling in the initial and final states is also uncertain, since the doubling observed in the band-lines represents a difference of two term-doublings. These uncertainties can probably be removed only by the analysis of band systems having terms in common with the bands here under discussion.

General remarks on term-notation, term-formulation, j values, etc. Hund's theory gives no explanation of the phenomenon of alternating intensities in band lines.[24a] Also it does not obviously account for the precise nature and selection rules which are observed in σ-type doubling, although it does predict correctly the presence or absence of such doubling. But at every point where the theory as so far developed is specific, all the experimental evidence appears to be in agreement with it.

The question of a systematic difference between the j numbering of even and odd molecules was not considered by Hund. In terms of the new quantum mechanics, the rotational energy for a σ-type term is given by $E^m = B[j(j+1) - \sigma^2] + \cdots$.[25] If this formulation is adopted, the experimental evidence[4,5,6,7,11] shows definitely that $j(j = \sigma, \sigma+1, \sigma+2, \cdots)$ is

[24] M. Fassbender, Zeits. f. Physik, **30**, 73 (1924); R. Mecke, ref. 18.

[24a] W. Heisenberg has recently presented a very interesting theory of alternating intensities (Zeits. f. Physik, Spring, 1927) in terms of the wave mechanics.

[25] This equation, obtained for the symmetrical rotator by D. M. Dennison (Phys. Rev., **28**, 318, 1926), Kronig and Rabi (Nature, **118**, 805 (1926), Phys. Rev. **29**, 262, 1927), and by F. Reiche (Zeits. f. Physik, **39**, 444, 1926), is doubtless also applicable here. Dennison does not decide between integral and half-integral j values, but Kronig and Rabi conclude that only integral values are allowable. This conclusion may well hold when σ corresponds to nuclear rotational energy, but in view of the experimental facts, evidently does not hold when σ is an electronic quantum number and *when s is present* with a half-integral value.

integral for even molecules and half-integral for odd molecules (the j values in the above formulation are all $\frac{1}{2}$ unit less than those used by the writer in previous papers). The same j values also hold in ρ-type terms, and doubtless in general.

In terms of Hund's theory, it is now apparent that the Kramers and Pauli rotational energy term $F(j)=Bm^2+\cdots=2B[(j^2-\sigma^2)^{1/2}-\rho]^2\cdots$, while formally capable of accounting for observed relations, is inappropriate physically, and should be replaced in Hund's cases (a) and (b) by Eqs. (1) and (2) above; in transition cases, the relation is more complicated. The variable electronic term in Eq. (2), which must also be present in transition cases, probably gives contributions[26] involving all powers of j. The contribution to the quadratic term probably accounts for the frequently rather large differences[4,11] between the apparent B values for the components of a ^2P or other multiple level; hitherto these have been interpreted as due to (unaccountably large) differences in moments of inertia, but recent work of Kemble and Jenkins[26] indicates that they can be accounted for quantitatively in terms of Hund's theory, with a single moment of inertia. The electronic contribution to the linear term in j also probably accounts in part (not wholly, since secondary ρ's occur even for singlet electronic states) for the frequent occurrence of apparent "secondary ρ's," whose existence is equivalent to the occurrence of a linear term in j; also, cf. Kemble, ref. 3, pp. 345–7.

The "effective rotational quantum number" T, defined in previous papers[5] as $j-\rho$, retains its meaning in Hund's case a (where $\rho=0$, $T=j$). In case (b), T might best be redefined as $T=j_k$; in the special case of ^2S states (where $j=j_k+\rho$, $\rho=\pm\frac{1}{2}$), this coincides with the previous definition. For transition cases between (a) and (b), the appropriate definition of T is not evident. When cases a and b are approximated, Eqs. 8E, 13, 14, and 15 of ref. 5, after dropping the terms in $\rho\sigma^2$, remain valid, in terms of T, for $F(j)$, $\Delta_1F(j)$, $\Delta_2F(j)$, and ν.

In terms of Hund's theory, it is evident that the notation ^1S, ^1P, ^2P, etc., as used in previous papers of this series, is far from identical in meaning with that for the line spectrum case. According to the theory, the molecular quantities s, σ_k, and σ in case (a) play the same part in molecular multiplets as do s, k, and j (Sommerfeld's j_s, j_a, and j) in ordinary atomic multiplets (but cf. ref. 2). The most notable difference is the distinction required between k and σ_k in the molecular case. Practically there is at present little evidence on which to base this distinction. Probably σ_k is identical with k in many or perhaps even in most of the familiar band spectra. When it becomes possible to determine both k and σ_k, such a notation as e.g. $^2P_1{}^D$ might be introduced to describe the case $k=2$, $\sigma_k=1$, $s=\frac{1}{2}$, $\sigma_s=-\frac{1}{2}$. In the mean time, the continued use of the simple designations $^2P_1$, ^1S, etc. would seem to be both appropriate and convenient for the empirical classification of molecular electronic terms.

WASHINGTON SQUARE COLLEGE,
NEW YORK UNIVERSITY,
February 12, 1927.

[26] E. C. Kemble and F. A. Jenkins, Bull. Am. Phys. Soc. **2**, No. 1, Abstr. No. 9 (Feb. 12, 1927).

SCREENING CONSTANTS FROM OPTICAL DATA

By O. Laporte

Abstract

Grotian identified the relativistic doublets which correspond to the ionization of an n_2 shell in the spectra of the rare gases. Similarly the doublets which belong to the n_3 shells are found in the spectra of 29 Cu, 45 Rh, and 79 Au. The different relative stability of the n_3 electrons as compared with the $(n+1)_1$ electrons is clearly noticeable in every one of the three long periods. The screening constants are in good agreement with those computed from x-ray data, even in cases where the "optical" screening constant is obtained from elements the outer shell of which is not yet complete.

THE similarity of the energy diagrams of the x-ray spectra and of the optical alkali-spectra was first pointed out by W. Grotrian[1] in 1922. It led Landé[2] to a complete identification of the x-ray terms as doublet terms according to the following diagram:

Table I

K_{11}	L_{11}	L_{21}	L_{22}	M_{11}	M_{21}	M_{22}	M_{32}	M_{33}
1^2S	2^2S	2^2P_1	2^2P_2	3^2S	3^2P_1	3^2P_2	3^2D_2	3^2D_3

in which the relativistic doublets appear as analogues of the magnetic complex structure, whereas the screening doublets seem to be caused by differences of the azimuthal quantum number. This analogy was used also by Sommerfeld[3] to compute intensities of x-ray line groups and by Wentzel[4] to predict the fine structure of the so-called x-ray spark lines. The complex structure of the x-ray energy diagram was finally made clear by the Russell-Hund theory of complicated spectra. It proved that on account of Pauli's[5] exclusion principle, when ionizing a shell of N electrons z times, the same energy states and quantum numbers appear as in an atom with z valence electrons. In other words: incomplete shells of z or $N-z$ electrons show the same terms, if N is the "Besetzungszahl" (2, 6, 10, 14, etc.). Since Kossel we are accustomed to regard the x-ray levels as the stationary states of a simply ionized shell and hence must expect doublet terms of similar structure as for the alkalis. We thus arrive at an explanation of Table I.

But with the help of the Bohr-Stoner theory of the periodic system we can also predict the elements where these x-ray terms must appear on the surface of the atom and will be noticeable as optical doublet terms. The ionized K-shell will give a 1^2S term for the normal state of He^+ and H and

[1] W. Grotrian, Zeits. f. Physik, **8**, 116 (1922). See especially footnote No. 3 on page 117.
[2] A. Landé, Zeits. f. Physik **16**, 391 (1923).
[3] A. Sommerfeld, Ann. d. Physik **76**, 284, (1925).
[4] G. Wentzel, Zeits f. Physik **31**, 445, (1925).
[5] W. Pauli, Zeits. f. Physik **31**, 765 (1925).

similarly we obtain a ^2S term as lowest term of the alkaline-earth ions or the neutral alkali atoms. When ionizing the complete L shell at 10Ne, the electrons will arrange themselves so as to yield a 2^2P term as lowest term of Ne^+ or of 9F. In the same way we will get 3^2P, 4^2P · · · terms as the normal states of the ions of 18A, 36Kr, · · · or of the neutral atoms of 17Cl, 35Br · · · respectively. Applying the same reasoning likewise to the higher subgroups we must expect ^2D terms with total quantum-number 3, 4, 5 at the end of the iron, palladium and platinum groups and finally a 4^2F term at the end of the rare earth group. Unfortunately the end of these shells is not so marked in the periodic table as the completions of the shells with azimuthal quantum number $k=1$ and 2; a more detailed discussion will be necessary to select the right elements, where one has to look for the x-ray terms in the optical region.

The above-mentioned appearance of the relativistic L-doublet in the spectrum of Ne^+ was first pointed out by Grotrian.[6] As is well known he identified it with the two series limits which Paschen[7] had found in the arc spectrum of Ne. Grotrian was also able to show, that the numerical value of Paschen's frequency difference agreed approximately with the separation computed with the Sommerfeld formula for relativistic doublets:

$$\frac{\Delta\nu}{R}=\frac{\alpha^2(Z-s)^4}{n^3j(j-1)} \tag{1}$$

if one inserts $Z=10$, $n=2$ and $j=2$. One can formulate this result as follows: substituting on the left side of this equation Paschen's empirical frequency difference for Ne and solving for the screening constant s, we obtain a value which is in close agreement with the value used for the representation of the relativistic doublets of the elements from $Z=13$ to $Z=92$. In his recent analysis of the arc spectrum of argon Meissner[8] found, that, in strict analogy to neon, the terms converge toward two limits which he identified as M_{21} and M_{22}. From this doublet separation Grotrian[9] computed the screening constants of this relativistic M doublet and compared it with that obtained from the x-ray spectra of the elements $Z=37$ to $Z=92$.

This latter note of Grotrian's suggested to me to try the same with the relativistic doublets appearing at the end of the three long periods, namely, the iron, palladium and platinum groups. The doublets in question are in the x-ray notation $M_{32}M_{33}$, $N_{32}N_{33}$, and $O_{32}O_{33}$; from the optical viewpoint they must appear respectively as 3^2D, 4^2D and 5^2D terms. As was mentioned before, the difficulty arises that the end of these n_3 shells is not so clearly noticeable—the "rare gas" at the end of these periods is evidently missing—the reason being that in each of the three shells two types of orbits furnish the lower terms.[10] In a shell made up of n_2 or p electrons (e.g. B−Ne,

[6] W. Grotrian, Zeits f. Physik **8**, 116, (1922).

[7] F. Paschen, Ann. d. Physik **60**, 405 (1919): **63**, 201 (1920).

[8] K. W. Meissner, Zeits. f. Physik **39**, 172 (1926).

[9] W. Grotrian, Zeits. f. Physik **40**, 10 (1926).

[10] For the following compare the author's paper on the complex spectra in Jour. Opt. Soc. Amer. **13**, 1 (1926).

Al−A, Ga−Kr etc.) the lowest terms arise from configurations with p electrons only (e.g. ^2P of all from one p, ^3P in Si from two p or (p^2) ^4S in P from (p^3) etc.) On the other hand the lowest terms of an element in the iron group may arise from both 4_1 and 3_3 and similarly for the next periods from 5_1 and 4_3 electrons. In Professor Russell's notation we may summarize the results of the spectral classifications with the statement that in the long periods the low energy states of atoms or ions with z valence electrons are configurations of the types $(d^{z-2}s^2)$ $(d^{z-1}s)$ and (d^z). Which of the three configurations will be so low as to furnish prominent combinations varies strongly for different elements and periods and cannot be predicted theoretically. Several empirical rules have been given to represent the facts;[11] the most obvious of them being that in higher spark spectra the influence of the s electrons will become smaller and terms of type (d^z) will prevail. As a consequence of Pauli's exclusion principle a shell of n_3 electrons becomes complete with the *tenth* electron. The problem therefore is to find ^2D terms arising from a configuration of type (d^9).

In order to find the doublet $M_{32}M_{33}$ in the first long period it seems reasonable to look for the term $^2D(d^9)$ in the arc spectrum of 27 Co. According to Bechert and Catalan,[12] however, the stable configurations of Co are of type (d^7s^2) and (d^8s), whereas configuration (d^9) seems to be very unstable. Another possibility of finding the term $^2D(d^9)$ would be in the spark spectrum of Ni. So far as we know no data on NiII have been published.[13] But we can find our relativistic doublet in the arc spectrum of the following element 29 Cu, which has recently been investigated by Shenstone and others.[14] Besides the normal state of Cu, $^2S(d^{10}s)$, there exists an inverted metastable term which was identified by Shenstone to be $^2D(d^9s^2)$. Its separation equals 2043 cm^{-1}. We shall use this term for the computation of the screening constant. The presence of two 4_1 electrons, i.e., of the complete N_{11} shell has no influence: using the configuration (d^9s^2) for our purpose we only approach and approximate the conditions under which x-ray spectra are observed.

In the second long period the d electrons (4_3) have gained so much in stability that terms of type (d^5)—without any 5_1 electrons—occur even in arc spectra. About a year ago the writer[15] identified a ^2D term as the sought-for $N_{32}N_{33}$ doublet in the arc spectrum of rhodium. Its separation is $\Delta\nu = 2348$ cm^{-1}. Also a ^2D term was found by McLennan and Smith[16] in the spark spectrum of palladium. This term, too, gives the right order of magnitude for the

[11] O. Laporte, Zeits. f. Physik, **39**, 123 (1926). Compare also the somewhat different viewpoint of L. A. Sommer, Zeits. f. Physik, **37**, 1 (1926).

[12] K. Bechert and M. A. Catalan, Zeits. f. Physik, **32**, 336 (1925).

[13] The term $^2D(d^9)$ probably corresponds to the normal state of Ni^+. Comp. O. Laporte, Zeits. f. Physik, **39**, 123 (1926).

[14] A. G. Shenstone, Phys. Rev. **28**, 449 (1926), C. S. Beals, Proc. Roy. Soc. **A111** (1926); L. A. Sommer, Zeits. f. Physik, **39**, 711 (1926).

[15] O. Laporte, Journ. Opt. Soc. Amer., **13**, 1 (1926). See especially p. 22

[16] J. C. McLennan and H. G. Smith, Proc. Roy. Soc. **A112**, 110 (1926).

screening constant. The separation given by McLennan and Smith is 3512 cm^{-1}.

As to the relative stability of d and s electrons, the third long period resembles the first period toward its end. It is, therefore, improbable that the $^2D(d^9)$ term will be found among the lower metastable terms of the arc spectrum of iridium ($Z=77$).[17] As was pointed out by Grimm and Sommerfeld,[18] the arc spectrum of gold resembles that of copper in the fact that s and d electrons are about equally stable, whereas in silver the s electrons exceed by far the d electrons in stability. Consequently one must expect a low metastable ^2D term belonging to the configuration (d^9s^2), which, indeed, was recently published by McLennan and McLay[19] in their second revised paper on Au. The separation of this term is 12274 cm^{-1}.

In Table II the screening constants s computed from the optical data[20] are compared with those of the x-ray spectra. Substituting the numerical values for R and α, and solving Eq. (1) for s, we have the formula:

$$s=Z-\left(\frac{n^3j(j-1)}{5.83}\Delta\nu\right)^{1/4} \tag{2}$$

which was used for the calculation of the s values.

At the top of the table the quantum numbers and the optical notation are given, on the left side the x-ray notation. The numbers in italics are the

TABLE II

Comparison of the screening constants computed from optical data with those of x-ray spectra.

Optical notation Sommerfeld's Indices Bohr's Indices	^2P 21—22 II—III	^2D 32—33 IV—V	^2F 43—44 VI—VII
L	$Z=17$ – 92 : *3.50* 9 F : 3.21 10 Ne : 3.20		
M	$Z=37$ – 92 : *8.5* 17 Cl : 7.50 18 A : 7.29	$Z=41$ – 92 : *13.0* 29 Cu : 13.60[21]	
N	$Z=53$ – 92 : *17.0* 35 Br : 18.13	$Z=51$ – 92 : *24.4* 45 Rh : 25.17 46 Pd : 24.07	$Z=81$ – 92 : *34* 71 Lu : ?
O	— — 53 I : 29.10	— — 79 Au : 45.55	

[17] The tentative identification of two levels in the iridium spectrum as ^2D by W. F. Meggers and O. Laporte (Phys. Rev. **28,** 642, 1926, vide p. 660) must probably be given up, since the $\Delta\nu$ of this term is much too small to be of the right order of magnitude.

[18] H. G. Grimm and A. Sommerfeld, Zeits. f. Physik, **36,** 36 (1926).

[19] J. C. McLennan and A. B. McLay, Proc. Roy. Soc. **A112,** 95 (1926).

[20] For the sake of completeness we include the screening constants computed from the data given by Turner, (Phys. Rev. **27,** 397, 1926) for Cl, Br, I, and by Bowen (Phys. Rev. **29,** 231, 1927) for the spectrum of F.

[21] Note added to proof: The fact that the ^2D term of Cu gives an s in agreement with that obtained from x-ray data has already been noted by A. G. Shenstone (Nature **116,** 467, 1925).

screening constants as obtained from the relativistic x-ray doublets, whereas underneath the optical screening constants are given together with the elements from whose spectrum they were obtained.

In general the agreement is rather good. The large fluctuation of the s values for $N_{32}N_{33}$ in the spectra of Rh and Pd is remarkable.[22] The largest deviation which is also discussed at length by Grotrian[9] occurs for the $M_{21}M_{22}$ doublet in A and Cl. Grotrian explains this disagreement as due to the incompleteness of the M shell at A. Since the x-ray screening constant is obtained from elements with atomic number 37 and larger, where the entire M shell is completed, we should expect a smaller s for elements with atomic number smaller than 29 (Cu). But we see from Table II that this cannot be true; for we would have to expect a still larger deviation $s_{\text{x-ray}}-s_{\text{opt.}}$ for the doublet $N_{21}N_{22}$, a somewhat smaller one for N_{32} N_{33} and good agreement for all the doublets which are last in their shells ($L_{21}L_{22}$, $M_{32}M_{33}$, $N_{43}N_{44}$). On the contrary we find $s_{\text{opt.}}>s_{\text{x-ray}}$ for $N_{21}N_{22}$ and fair agreement for $N_{32}N_{33}$ although the whole N shell does not become complete until after the rare earths ($Z>71$). We consequently arrive at the conclusion that the value of the screening constant of a Stoner sub-group is independent of the presence of the sub-groups with higher azimuthal quantum k and that the relatively large positive and negative deviation of the optical and x-ray values are apparently due to irregular local disturbances.

Unfortunately the s value for $N_{43}N_{44}$ cannot yet be obtained from optical data, since the spectra at the end of the rare earth group have not been investigated. With the (very inaccurate) value 34 from x-ray data we obtain for the terms ${}^2F(f^{13})$, ${}^2F(f^{13}s^2)$ and also ${}^3F(f^{13}s)$ which we have to expect among the low metastable terms of 70 Yb, a separation of about 13,000 wave number units.

On the other hand we are able to predict screening constants for the O doublets.[23] Attempts are being made at this laboratory to separate the O_{21} and O_{22} levels for the heaviest elements.

DEPARTMENT OF PHYSICS
UNIVERSITY OF MICHIGAN,
February 25, 1927.

[22] Compare the similar fluctuations of the s of the L-doublet near $Z=26$, which were pointed out by D. M. Bose, Phys. Rev. **27**, 521 (1926).

[23] A. Sommerfeld (Journ. Opt. Soc. **7**, 503, 1923) shows that the screening constants with the exception of that of the L-doublet, are integer multipla of 4.2. The two new values of the O-screening constants are also respectively 7 and 10 times this constant.

MULTIPLETS IN THREE ELECTRON SYSTEMS OF THE FIRST LONG PERIOD

By R. C. Gibbs and H. E. White

Abstract

Wave-lengths and relative positions of multiplets in the spectra of Sc (I), Ti (II), V (III), and Cr (IV).—Using the regular and irregular doublet laws as guides, it has been found possible, from the corresponding known multiplets in Sc (I) and Ti (II), to identify the triad of multiplets of V (III) designated as $^4F_{2,3,4,5}-{}^4G_{3,4,5,6}$; $^4F_{2,3,4,5}-{}^4F'_{2,3,4,5}$; and $^4F_{2,3,4,5}-{}^4D_{1,2,3,4}$. For these multiplets the initial state is given by one *4p* electron and two *3d* electrons. In the final state the *4p* electron has shifted to a *4s* orbit. The separations of the $^4F_{2,3,4,5}$ levels are found to be in the ratio 2.50:3.52:4.50, in very close agreement with Landé's interval rule. The relative intensities of the lines in these multiplets conform to the usual rule. A comparison of the data for one, two, and three electron systems of Sc, Ti, and V shows that the addition of first one and then a second *d* electron causes not only an increase in the multiplicity but also successive shifts in the radiated lines toward the longer wave-lengths by very nearly the same frequency interval. It has also been found possible to identify the $^4F_{2,3,4,5}-{}^4F'_{2,3,4,5}$ multiplet of Cr (IV).

IT HAS been shown[1] that for the one electron systems of the first long period from K(I) to Mn(VII) the first lines of the principal series follow very closely the regular and irregular doublet laws. Each of these lines results from an electron in a *4p* orbit jumping into a *4s* orbit. Similarly for two electron systems of this same period from Ca(I) to Cr(V), we have been able to show that when one of the electrons in a *4p* orbit jumps to a *4s* orbit in the presence of an electron in a *3d* orbit a triad of multiplets of the type $^3D_{1,2,3}-{}^3P_{0,1,2}$, $^3D_{1,2,3}-{}^3D'_{1,2,3}$, and $^3D_{1,2,3}-{}^3F_{2,3,4}$, also follow the regular and irregular doublet laws.[2]

In the three electron systems Sc(I), Ti(II), and V(III), three multiplets forming a triad of the type $^4F_{2,3,4,5}-{}^4D_{1,2,3,4}$; $^4F_{2,3,4,5}-{}^4F'_{2,3,4,5}$; and $^4F_{2,3,4,5}-{}^4G_{3,4,5,6}$, have been identified which obey these same laws. For these multiplets the initial state is given by one *4p* electron and two *3d* electrons. The final state finds one electron in a *4s* orbit and the other two in *3d* orbits. This transition may have taken place in two ways either by a one electron jump, *4p* to *4s*, or by a two electron jump, *4p* to *3d* and *3d* to *4s*. If the two electron jump takes place one electron has changed by $\Delta k=1$, and the other by $\Delta k=2$.

In either case the sums of the total quantum numbers for the initial and final states are equal, which is the necessary requirement that the resultant spectral lines follow the doublet laws.

Multiplets in the arc spectrum of scandium have been itendified by Catalan.[3] He reports three multiplets of the type $^4F_{2,3,4,5}-{}^4D_{1,2,3,4}$, $^4F_{2,3,4,5}$

[1] R. C. Gibbs and H. E. White, Nat. Acad. Sci. Proc. **12**, 448 (1926).
[2] R. C. Gibbs and H. E. White, Phys. Rev. **29**, 426 (1927).
[3] Catalan, Ann. de Soc. Esp. Fis. Y Quim. p. 466 (Nov., 1923).

$-{}^4F'_{2,3,4,5}$, and ${}^4F_{2,3,4,5}-{}^4G_{3,4,5,6}$, in the region of 5000A.U. The intensities, wave-lengths, and frequencies of the lines in these multiplets as well as the relative term values are given in Table I. In Ti(II) a similar triad of the

TABLE I

Multiplet Triad in Sc(I) (*Catalan*)

$d^2p \rightarrow d^2s$

		${}^4F_5$		${}^4F_4$		${}^4F_3$		${}^4F_2$
		157.3	(67.1)	90.2	(52.5)	37.7	(37.7)	000
		200						
		5671.83						
${}^4G_6$	17783.3	17626.1						
	(113.6)	15		150				
		5708.63		5686.83				
${}^4G_5$	17669.7	17512.5		17579.6				
	(93.6)	2		15		100		
		5739.21		5717.29		5700.18		
${}^4G_4$	17576.1	17418.9		17486.0		17538.4		
	(73.2)			1		15		100
				5741.34		5724.08		5711.75
${}^4G_3$	17502.9			17412.7		17465.2		17502.9
		125		10				
		5081.57		5064.32				
${}^4F'_5$	19830.7	19673.5		19740.5				
	(75.3)	20		90		40		
		5101.08		5083.70		5070.21		
${}^4F'_4$	19755.4	19598.2		19665.3		19717.6		
	(59.6)			40		60		10
				5099.20		5085.53		5075.81
${}^4F'_3$	19695.8			19605.5		19658.2		19695.8
	(43.3)					30		50
						5096.72		5086.99
${}^4F'_2$	19652.5					19615.0		19652.5
		40		8		0		
		4743.80		4728.77		4717.03		
${}^4D_4$	21231.5	21074.3		21141.2		21193.9		
	(54.6)			30		10		0
				4741.02		4729.21		4720.77
${}^4D_3$	21176.9			21086.6		21139.3		21177.1
	(37.6)					18		10
						4737.65		4729.21
${}^4D_2$	21139.3					21101.7		21139.3
	(21.8)							15
								4734.10
${}^4D_1$	21117.5							21117.5

same type in the region of 3000A.U. has been reported by Russell,[4] and by Meggers, Kiess, and Walters.[5] Their results are shown in Table II together with the relative values of the ${}^4F_{2,3,4,5}$, ${}^4D_{1,2,3,4}$, ${}^4F'_{2,3,4,5}$, and ${}^4G_{3,4,5,6}$ terms

[4] H. N. Russell, Astrophys. Jour. **61**, 254 (1925).

[5] Meggers, Kiess and Walters, J.O.S.A. **9**, 364 (Oct., 1924)

where the $^4F_2$ term, which is the lowest level of the normal state of the ionized atom, is taken as zero. Applying the irregular doublet law, i.e. a

TABLE II

Multiplet Triad in Ti(II)[4,5]

$d^2p \rightarrow d^2s$

		$^4F_5$	$^4F_4$	$^4F_3$	$^4F_2$
		393.3 (167.7)	225.6 (131.5)	94.1 (94.1)	000
		40			
		3349.41			
$^4G_6$	30240.6	29847.4			
	272.5	15	40		
		3380.28	3361.22		
$^4G_5$	29968.1	29574.9	29742.6		
	233.6	4	15	30	
		3407.20	3387.83	3372.80	
$^4G_4$	29734.5	29341.3	29509.0	29640.4	
	190.0		5	15	40
			3409.80	3394.57	3383.76
$^4G_3$	29544.5		29318.9	29450.4	29544.5
		60	15		
		3234.52	3217.04		
$^4F'_4$	31300.9	30907.6	31075.5		
	187.4	20	50	15	
		3254.23	3236.57	3222.82	
$^4F'_3$	31113.5	30720.4	30888.0	31019.8	
	154.8		25	40	15
			3252.85	3239.03	3229.18
$^4F'_2$	30958.7		30733.5	30864.6	30958.7
	122.1			20	40
				3251.89	3241.97
$^4F'_1$	30836.6			30742.5	30836.6
		60	30		
		3088.03	3072.10	?	
$^4D_4$	32767.3	32373.9	32541.7		
	69.1		45	30	
			3078.64	3066.20	?
$^4D_3$	32698.2		32472.6	32604.3	
	95.6			40	20
				3075.22	3066.36
$^4D_2$	32602.6			32508.7	32602.6
	70.1				40
					3072.97
$^4D_1$	32532.5				32532.5

linear extrapolation of ν from each multiplet in Sc(I) and Ti(II), the corresponding multiplets were looked for in the spark spectrum of vanadium in the vicinity of 2500A.U. Three very strong multiplets have been identified in this part of the spark spectrum, the details for which are given in Table III. The wave-lengths in Tables I and II are given in I.A.(air) while those in

Table III are in I.A.(vac). Assuming the regular doublet law to hold an extrapolation from the values of the $^4F_{2,3,4,5}$ separations for Sc(I), and Ti(II) enabled us to predict the $^4F_{2,3,4,5}$ separations for V(III) to be about

TABLE III

Multiplet Triad in V(III)
$d^3p \rightarrow d^3s$

		$^4F_5$	$^4F_4$	$^4F_3$	$^4F_2$
		705.1 (301.7)	403.4 (235.8)	167.6 (167.6)	000
		200			
		2371.76			
$^4G_6$	42867.6	42162.8			
	(503.1)	75	150		
		2400.40	2383.18		
$^4G_5$	42364.5	41659.7	41960.7		
	(431.0)	2	80	125	
		2425.51	2407.90	2394.27	
$^4G_4$	41933.5	41228.4	41530.0	41766.4	
	(351.6)		2	40	100
			2428.43	2414.62	2404.89
$^4G_3$	41581.9		41178.8	41414.4	41581.9
		100	50		
		2331.09	2314.81		
$^4F'_5$	43603.2	42898.4	43200.1		
	(325.8)	30	75	40	
		2348.94	2332.39	2319.65	
$^4F'_4$	43277.4	42572.4	42874.5	43109.9	
	(281.0)		30	75	40
			2347.78	2334.87	2325.78
$^4F'_3$	42996.4		42593.4	42829.0	42996.3
	(221.3)			30	75
				2347.00	2337.80
$^4F'_2$	42775.1			42607.6	42775.1
		70	25	2	
		2233.46	2218.49	2206.96	
$^4D_4$	45479.2	44773.6	45075.7	45311.2	
	(39.9)		40	20	2
			2216.55	2205.00	2196.88
$^4D_3$	45519.1		45115.2	45351.5	45519.1
	(267.7)			30	8
				2218.09	2209.88
$^4D_2$	45251.4			45083.8	45251.4
	(186.9)				30
					2219.04
$^4D_1$	45064.5				45064.5

$\Delta\nu = 172$, 246, and 310. These separations are found to be $\Delta\nu = 167.6$, 235.8, and 301.7 which is in very close agreement with the predicted values. According to Lande's interval rule these separations should have values in the ratio 2.5:3.5:4.5. The observed separations are in the ratio 2.50:3.52:4.50.

Owing to insufficient data on chromium in the extreme ultra-violet we have as yet been able to identify with certainty only the ${}^4F_{2,3,4,5}-{}^4F'_{2,3,4,5}$ multiplet and several lines of the ${}^4F_{2,3,4,5}-{}^4G_{3,4,5,6}$ multiplet.

The linear progression in frequency of each of the above multiplets with the atomic number, is brought out most clearly in Fig. 1 for the first three

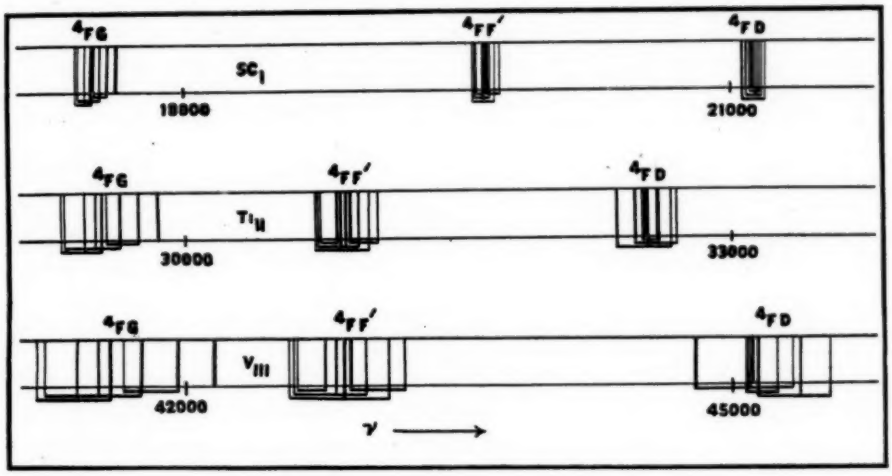

Fig. 1. Three electron systems of the first long period.

elements. It may be seen that by displacing the frequencies of each group of lines to the left by $\Delta\nu=12{,}000$ with respect to the spectral groups of the element just preceding it, corresponding multiplets are seen to lie very nearly one below the other. In this way the small departures from the irregular doublet law appear to be magnified.

The increasing frequency separations of the ${}^4F_{2,3,4,5}$ levels, as may be seen in Fig. 1 follows directly from the regular doublet law which requires that $\Delta\nu=K(Z-s)$.[4] This law although derived for doublet separations is found to apply also to multiplet terms.[2] The screening constants as computed from the above relation are given in Table IV. If Fig. 1 had been

TABLE IV

Regular doublet laws

	$\Delta\nu$ ${}^4F_5-{}^4F_4$	$(\Delta\nu/.0456)^{1/4}$	s	$\Delta_1\lambda$ $({}^4F_5F'_5-{}^4F_4F'_5)$	$\Delta_2\lambda$ $({}^4F_5F'_5-{}^4F_5F'_4)$
Sc(I)	67.1	6.193	14.807	17.25	19.51
Ti(II)	167.7	7.787	14.213	17.48	19.71
V(III)	301.7	9.018	13.982	16.28	17.85

plotted to a scale of wave-lengths in place of frequencies, the corresponding ${}^4F_{2,3,4,5}$ separations would have been almost the same for each multiplet in all three elements. This is also a consequence of the regular doublet law. This constancy of $\Delta\lambda$ between corresponding lines in each of these multiplets

is quite remarkable. Examples of this are given in the last two columns of Table IV. There are in a few cases departures from this rule just as there are occasional departures from the interval rule as given by Landé for term separations.

Starting with the one electron system of any of the elements given in Table V, it is seen that the screening effect due to the addition of first one

TABLE V

Screening effect of d electrons.

Doublets $p \rightarrow s$ $4^2S_1 - 4^2P_2$		Triplets $dp \rightarrow ds$ $a^3D_3 - a^3F_4$		Quartets $d^2p \rightarrow d^2s$ $a^4F_5 - a^4G_6$
Sc(III)		Sc(II)		Sc(I)
37039.6	(9376.0)	**27663.6**	(10037.5)	**17626.1**
(11311.2)		(12070.1)		(12221.3)
Ti(IV)		Ti(III)		Ti(II)
48350.8	(8617.1)	**39733.7**	(9886.3)	**29847.4**
(11163.6)		(11837.7)		(12315.4)
V(V)		V(IV)		V(III)
59514.4	(7943.0)	**51571.4**	(9408.6)	**42162.8**
(11020.9)		(11994.9)		(12181.5)
Cr(VI)		Cr(V)		Cr(IV)
70535.3	(6969.0)	**63566.3**	(10778.0)	**54344.3**

and then a second d electron is to shift the spectral lines toward the longer wave-lengths by very nearly the same frequency interval, while at the same time the multiplicity is increased. The uniformity of this shift is more strikingly brought out in Fig. 2 where in passing downward along any of the light diagonals there is a successive addition of d electrons with a simultaneous decrease in effective core charge. Fig. 2 also serves to bring out the nearly linear displacement of multiplets when successive d electrons are added keeping the effective core charge nearly constant i.e. upward along the heavy diagonals. The irregular doublet law which holds here for isoelectronic systems, is illustrated by the almost equal intervals along the verticals. To show this screening effect, we have taken the strongest line in each electron system as representing the position in the spectrum of that system of lines. In the one electron systems the $4^2S_1 - 4^2P_2$ line is the strongest line of the doublet since k and j are changing in the same direction. For the two electron systems the strongest line of all three multiplets is the line $^3D_3 - {}^3F_4$. Similarly for the three electron systems the line $^4F_5 - {}^4G_6$ is the strongest.

It is interesting to note that in general the jump from the multiple level having the largest k value into a common lower multiple level gives the strongest lines in the triad of multiplets; the intensities of the other multiplets following in an order corresponding to their relative k values. In each multiplet the stronger lines appear where k and j are changing in the

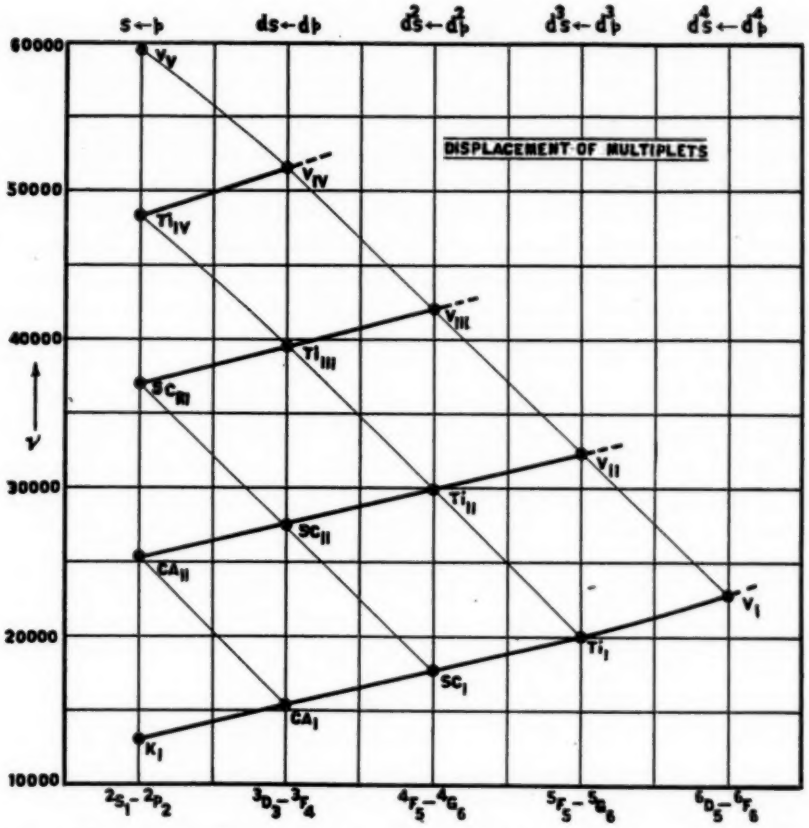

Fig. 2. Up heavy diagonals: successive addition of d electrons with constant core charge. Down light diagonals: successive addition of d electrons with simultaneous decrease in core charge. Up verticals: iso-electronic systems with successive increase in core charge.

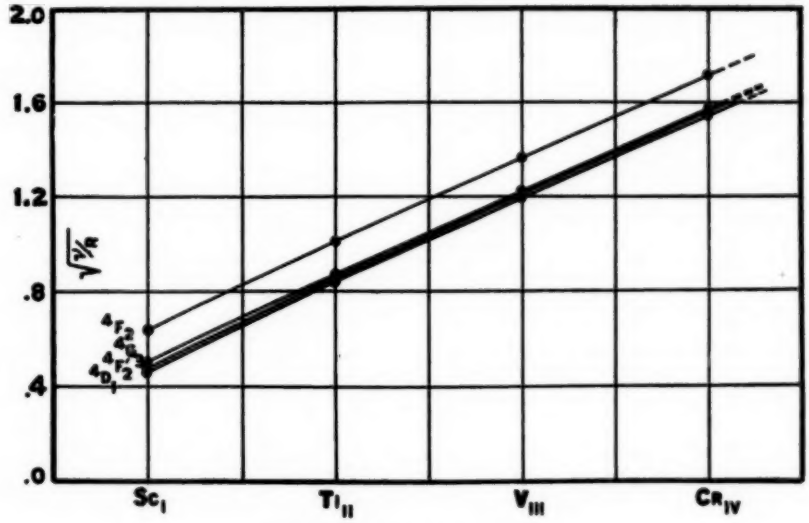

Fig. 3. Moseley diagram.

same direction. Of these stronger lines, which in Tables I, II and III are on the diagonals of each multiplet, the strongest line occurs for the transition involving the largest j values. From these intensity rules then it may be deduced that for a given electron configuration the most stable state occurs when the orbital axes and also the spin axes of all the valence electrons are as nearly as possible in the same direction. Furthermore when an electron transition takes place the most probable transition will be such that these axes retain as nearly as possible the same relative directions. The exceptions to this rule are probably accounted for, by ones inability to measure accurately the relative intensities of lines taken from different photographic plates, or from the failure of photography in general to record true relative intensities.

The lines on the Moseley diagram, Fig. 3, being parallel are a direct consequence of the irregular doublet law which requires $\Delta(\nu/R)^{1/2} = \text{constant}$, where ν is given in cm^{-1}. The values of $(\nu/R)^{1/2}$ were obtained by an extrapolation from terms already known in K(I), Ca(II), and Ca(I), Sc(II). It may here be pointed out that the regular and irregular doublet laws give an effective method of attack in the classification of spectra arising from higher states of ionization in iso-electronic systems of successive elements in any one Period.

CORNELL UNIVERSITY
January 27, 1927.

THE ABSORPTION SPECTRA OF Ga, In, Mn, Cr, Ni and Co IN UNDER-WATER SPARKS

By Alpheus W. Smith and Morris Muskat

Abstract

The absorption of gallium, indium, manganese, chromium, nickel and cobalt has been studied in under-water spark spectra. Many new lines, not previously found in absorption spectra, have been located. The results confirm and extend the observations on the absorption of these elements in the vapor state. For indium and gallium they confirm the conclusion that the normal state of the atom is the $2p$ state and for manganese, the conclusion that the ground level of the valence electron is the $1s$ septet level. For chromium, nickel and cobalt they afford a verification of the assignment of lines and arrangement of terms with respect to the ground level as given by Catalan and Gieseler for chromium, by Bechert and Sommer for nickel and by Catalan and Bechert for cobalt.

Introduction

A STUDY of the line absorption spectra of the different elements has become important in view of the information which it affords concerning atomic structure, especially the normal state of the last valence electron of the neutral atom. One of the principal methods of obtaining line absorption spectra of metals consists in observing the spectra which are emitted from oscillatory discharges passed between two metallic electrodes, immersed in water. Under these conditions, if oscillatory discharges of sufficiently high frequency are used, the spectrum of the metal consists of a continuous background on which the arc lines appear as reversed lines. Since it is the arc lines which are absorbed by the neutral atom, the lines which are reversed in the under-water spark give the same kind of information with respect to the neutral atom as is obtained by observing the absorption produced by a vapor of the metal in its normal state. Hence this method of obtaining absorption spectra of metals offers a means of extending and verifying results obtained by passing light through the normal vapor of the metal.

The absorption spectra of a large number of metals have previously been examined in under-water sparks. Finger[1] made the first important study of such spectra for seventeen metals. L. and E. Bloch[2] made similar observations on many of the same metals studied by Finger and extended the observations to some additional metals. Hulburt[3] also made similar observations on many metals studied both by Finger and L. and E. Bloch and on some additional metals but the results are not interpreted in terms of spectral series. Buffam and Ireton[4] and Clark and Cohen[5] continued this work, extending it to

[1] Finger, Zeits. f. wiss. Photo., **7**, 329 and 369 (1909).
[2] L. and E. Bloch, C. R. **174**, 1456 (1922). Jour. de Phys. et Rad. (3), **6**, 308 (1922).
[3] Hulburt, Phys. Rev. (2), **24**, 129 (1924).
[4] Buffam and Ireton, Roy. Soc. Can. Trans. (3), **19**, 113 (1925).
[5] Clark and Cohen, Roy. Soc. Can. Trans. (3), **20**, 1 (1926).

shorter wave-lengths and adding some elements not previously studied. The work of Clark and Cohen is devoted to the palladium-platinum group of metals.

The series relationships which have been recently worked out for a number of elements give a new meaning to such observations on line absorption. The recent work of Sur[6] on iron, and of Stucklen[7] on copper and cadmium suggests the importance of a more intensive study of some of the elements previously examined in order to obtain information concerning the corectness of the present assignment of the lines in spectral series and the arrangement of energy levels in the atom.

Experimental Method

The arrangement of the apparatus (Fig. 1) was similar to that used by Hulburt.[3] The condenser C was charged by means of a 20 kv 2.5 kw Thordarson transformer and then discharged through an auxilliary spark gap S

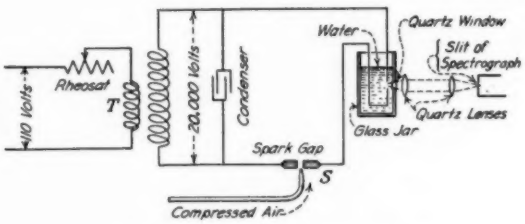

Fig. 1. Diagram of apparatus.

and the under-water spark in series. To insure an abrupt discharge compressed air was forced between the terminals of the auxilliary spark gap S. The primary of the transformer was connected to the 60-cycle, 110-volt-mains. The electrodes of the under-water spark were made of the metal whose absorption spectrum was being examined. Radiation from the under-water spark passed directly through the quartz window in the side of the glass jar and then through two quartz lenses by means of which it was brought to a focus on the slit of a Fery quartz spectrograph. The spectrum thus obtained was essentially continuous except for the absorption lines which belong to the arc spectrum of the metal from which the electrodes were made. Absorption lines due to the water were also observed and it is possible that a few absorption lines which do not belong to the arc spectrum of the metal may have been present.

For the ultra-violet region of the spectrum between about 2400A and 2100A distilled water was used in the jar. By refilling the jar with fresh distilled water several times during a single exposure it was possible under favorable conditions to photograph the spectrum as far as 2100A. For the region of the spectrum between the visible and about 2400A ordinary tap water was circulated rapidly through the jar. Care was taken to vary the

[6] Sur, Phil. Mag. (7), **1**, 433 (1926).
[7] Stucklen, ZS. f. Phys., **30**, 24 (1924); **34**, 8 (1925).

conditions of excitation by varying the inductance and capacity to bring out the maximum number of absorption lines. The times of exposure ranged from a few seconds for the visible portions of the spectrum to several minutes for the extreme ultra-violet.

The wave-lengths of the absorption lines were determined by comparison with the wave-lengths of the emission lines in the spectrum of the copper arc which was always photographed on the same film as the absorption spectrum of the metal in the under-water spark. The distances of the absorption lines from each other and from the known lines in the emission spectrum of copper were measured with a travelling microscope and the unknown wave-lengths calculated in the usual manner. It was possible thus to identify the absorption lines with certainty.

Experimental Results

Indium. The absorption of indium in the normal vapor is known from the work of Grotrian,[8] Rao[9] and Frayne and Smith.[10] Its absorption has not been previously studied in the spectra of under-water sparks. The observed wave-lengths for which absorption occurs in the under-water spark are recorded in Table I. It is noticed that those lines are found which are to be

Table I

Absorption spectrum of indium.

$\nu = 2p_2 - ms$			$\nu = 2p_2 - md$			$\nu = 2p_1 - ms$			$\nu = 2p_1 - md_{1,2}$		
λ	m	Notes	λ	m	Notes	λ	m	Notes	λ	m	Notes
4101.72	2	1,2,3	3039.34	3	1,2,3	4511.27	2	1,2,3	3258.52*	3	1,2,3
2753.87	3	1,2,3	2560.16	4	1,2,3	2932.60	3	1,2,3	56.03*	3	1,2
2460.06	4	1,2,3	2389.56	5	1,2,3	2601.75	4	1,3	2713.95	4	1,2,3
						2468.01	5	1,3	10.28	4	1,2
						2399.25	6	1,3	2522.99*	5	1,2,3
									2521.36*	5	1,2
									2430.7	6	1,3
									29.68	6	1,4
									2379.66†	7	

* Lines unresolved but both seem to be present
† New lines
[1] Grotrian in vapor
[2] Rao in vapor
[3] Frayne and Smith in vapor
[4] Not found by authors in under-water spark.

expected from the series relationship and from previous observations on the absorption of light by the normal metallic vapor. A number of lines which have been previously observed as absorption lines in the vapor of indium were not found. These lines are with two exceptions in the far ultra-violet where the intensity of the spectrum from the under-water spark is too small for satisfactory observations. Besides these recorded lines two unclassified lines (λ2957.02 and λ2836.90) were observed. The recorded wave-lengths are those used by Fowler.[11]

[8] Grotrian, ZS. f. Phys., **12**, 218 (1922).
[9] Rao, Phys. Soc. Lond. Proc., **37**, 259 (1924).
[10] Frayne and Smith, Phys. Rev. (2), **27**, 23 (1926).
[11] Fowler, Report on Series in Line Spectra, pp. 158–9.

Gallium. Because of the low melting point of gallium it was necessary to use it in the form of a gallium-tin alloy. The absorption spectrum of tin was first examined in the under-water spark. Then the absorption spectrum of the alloy of gallium and tin was studied. By the elimination of the absorption lines of tin from the spectrum of the alloy, the identification of the absorption lines of gallium was made possible. The absorption of the normal vapor of gallium is known from the work of Grotrian[8] and Frayne and Smith.[10] Table II shows the results. The recorded wave-lengths of gallium are those given by Klein.[12] For the shorter wave-lengths where the intensity of the under-water spectrum is small some wave-lengths previously observed as

TABLE II

Absorption spectrum of gallium

$\nu=2p_2-ms$			$\nu=2p_2-md$			$\nu=2p_1-ms$			$\nu=2p_1-md_{1,2}$		
λ	m	Notes	λ	m	Notes	λ	m	Notes	λ	m	Notes
4032.98	2	1,2	2874.24	3	1,2	4172.06	2	1,2	2944.18*	3	1,2
2659.87	3	2	2450.08	4	2	2819.66	3	2	43.7*	3	1
2371.33	4	2	2294.20	5	2	2418.70	4	2	2500.71	4	2
2255.03	5	2	18.04	6	2	2297.87	5	2,3	2338.60	5	2
						36.10	6	2,3	2259.23	6	2,3

* Lines unresolved but both seem to be present
[1] Grotrian in vapor
[2] Frayne and Smith in vapor
[3] Not found by authors in underwater spark.

absorption lines in the vapor were not located. This failure as in the similar case of indium is to be attributed to the faintness of the lines in that region of the spectrum. Except for this difference these observations confirm those made on absorption in the vapor.

Manganese. The electrodes were made of commercially pure manganese ground to suitable dimensions. The emission spectrum of managanese is known from the work of Catalan[13] and Fuchs.[14] In Table III these wave-

TABLE III

Absorption spectrum of manganese.

λ	Combination	Notes	λ	Combination	Notes
4032.49	$1^6S_3-1^6P_3$	1,2	2605.70	$1^7S_3-1^7P_2$	†
33.07	$1^6S_3-1^6P_2$	1,2	2593.72	$1^7S_3-1^7P_3$	†
30.76	$1^6S_3-1^6P_4$	1,2	2576.80	$1^7S_3-1^7P_4$	†
2801.08	$1^6S_3-2^6P_2$	1,2	2221.80	$1^6S_3-3^6P_2$	1
2798.27	$1^6S_3-2^6P_3$	1,2	13.80	$1^6S_3-3^6P_3$	1
2794.82	$1^6S_3-2^6P_4$	1,2	08.73	$1^6S_3-3^6P_4$	1

† New lines
[1] Zumstein in vapor
[2] Grotrian in vapor

lengths have been recorded out to two decimal places. The notation of the series classification has been modified to conform to modern usage. Table III

[12] Klein, Astrophys. Jour. **56**, 373 (1922).
[13] Catalan, Phil. Trans. A, **223**, 127 (1922).
[14] Fuchs, ZS. f. wissensch. Phot. **14**, 263 (1914).

shows a comparison of the absorption of manganese in the under-water spark and its absorption in the vapor phase. Both Grotrian[15] and Zumstein[16] have studied the line absorption of manganese in the vapor state. No previous observations on the absorption spectrum of manganese in under-water sparks are available. Grotrian observed absorption at six wave-lengths as indicated in Table III. Zumstein found a large number of additional absorption lines but for the sake of brevity only a few of these have been included in Table III. Many of them have wave-lengths which are too short to come within the region of these observations.

It will be seen from Table III that the three prominent triplets which Zumstein found to be absorbed in the vapor are also absorbed in the under-water spark. In addition to these triplets there is found the triplet $1^7S_3 - 1^7P_{2,3,4}$, which both Catalan and Back[17] have attributed to singly ionized manganese. According to de Gramont[18] these lines are *raies ultimes* in the spark spectrum of manganese. If these lines are correctly attributed to the singly ionized atom of manganese, they are the only absorption lines found in these observations on under-water absorption spectra which did not arise from the neutral atom. Stucklen[7] seems to have found absorption by singly ionized cadmium in a under-water spark.

On account of the brittleness of the manganese the under-water spark did not behave as well as it did in the case of the other metals. This fact doubtless accounts for the failure to observe as many absorption lines for manganese in the under-water spark as were observed by Zumstein in the vapor.

Chromium. The wave-lengths in Table IV are from papers on the arc spectrum of chromium by Catalan[19] and Gieseler.[20] The series combinations are taken either directly from Gieseler or when the multiplets are given only by Catalan his notation is changed to that of Gieseler in which the superscript at the left of the letter gives the multiplicity of the term and the subscript at the right of the letter gives the inner quantum number. The absorption of chromium vapor has been studied by Gieseler and Grotrian[21] and by Zumstein.[22] Observations on the absorption spectra in the underwater sparks are available from the work of Finger[1] and Hulburt.[3] Two prominent triplets have been found in the vapor and in the under-water spark. A third triplet further removed toward the ultra-violet was observed by Zumstein in chromium vapor. It is found here in the under-water spark spectrum. A large number of new absorption lines are also found. They are in agreement with the series combination given by Gieseler and Catalan. Besides these lines a number of unclassified lines were observed. These were distributed throughout the spectrum.

[15] Grotrian, ZS. f. Phys., **18**, 169 (1923).
[16] Zumstein, Phys. Rev. (2), **26**, 765 (1925).
[17] Back, ZS. f. Phys., **15**, 206 (1923).
[18] de Gramont, C.R. **171**, 1106 (1920).
[19] Catalan, Anales de Fisica Y Quimiea, **21**, 84 (1923).
[20] Giesler, ZS. f. Phys., **22**, 228 (1924).
[21] Grotrian and Giesler, ZS. f. Phys., **22**, 245 (1924).
[22] Zumstein, Phys. Rev. (2), **27**, 562 (1926).

TABLE IV

Absorption spectrum of chromium

λ	Combination	λ	Combination	λ	Combination	λ	Combination
4964.92	$4^5S_2-4a^7P_3$	3853.19	$4^5D_4-4b^5P_3$	3013.72	$4^5D_1-5a^5P_2$	2690.26	$4^5D_2-6^5F_3$
4829.36	———	31.03	$4^5D_3-4b^5P_3$	13.04	$4^5D_2-5a^5P_1$	84.72	$4^5D_4-6^5F_5$
4652.17	$4^5D_3-4a^5P_3$	22.08	$4^5D_2-4b^5P_3$	2996.58	$4^5D_2-2(II)^5D_j$	84.31	$4^5D_3-6^5F_3$
51.30	$4^5D_2-4a^5P_1$	14.62	$4^5D_1-4b^5P_1$	95.79	$4^5S_2-5a^5P_1$	82.52	$4^5D_3-6a^5P_3$
26.19	$4^5D_1-4a^5P_1$	06.70	$4^5D_2-4b^5P_2$	94.07	$4^5S_2-5a^5P_2$	80.74	$4^5D_2-6^5F_4$
13.37	$4^5D_0-4a^5P_1$	3615.65	———	91.90	$4^5D_1-1(II)^5D_j$	78.15	$4^5D_2-6^5F_2$
00.75	$4^5D_2-4a^5P_2$	05.33*	$4^7S_3-4a^7P_2$	88.67	$4^5S_2-5a^5P_2$	71.07	$4^5D_2-6a^5P_1$
4591.40	$4^5D_1-4a^5P_2$	3593.48*	$4^7S_3-4a^7P_3$	85.99	$4^5D_2-4(II)^5D_j$	70.52	$4^5D_2-6a^5P_2$
80.06	$4^5S_2-4a^5P_1$	78.69*	$4^7S_3-4a^7P_4$	85.86	$4^5D_2-3(II)^5D_j$	69.38	$4^5D_2-6a^5P_3$
65.53	———	10.53	———	80.79	$4^5D_0-2(II)^5D_j$	62.78	$4^5D_1-6a^5P_1$
46.04	$4^5S_2-4a^5P_2$	3494.96	———	75.48	$4^5D_1-3(II)^5D_j$	62.21	$4^5D_1-6a^5P_2$
14.53	———	81.30	———	71.11	$4^5D_2-4(II)^5D_j$	58.52	$4^5D_0-6a^5P_1$
4496.86	$4^5S_2-4a^5P_2$	60.43	———	67.64	$4^5D_2-5(II)^5D_j$	38.90	———
29.45	$4^5D_2-4^5F_2$	3266.55	$4^5D_4-5^5P_j$	11.14	$4^5D_4-4(III)^5D_j$	18.28	———
4391.76	$4^5D_2-4^5F_2$	44.14	$4^5D_2-5^5D_j$	10.90	$4^5D_2-5(III)^5D_j$	2591.86	$4^5D_4-n^5P_3$
84.98	$4^5D_4-4^5F_4$	3065.07	———	05.49	$4^5D_1-1(III)^5D_j$	77.66	$4^5D_3-n^5P_3$
73.27	$4^5D_3-4^5F_1$	53.88	$4^5D_4-5a^5P_3$	2899.21	$4^5D_1-2(III)^5D_j$	71.76	$4^5D_3-n^5P_2$
71.28	$4^5D_3-4^5F_3$	37.05	$4^5D_4-5^5F_4$	93.26	$4^5D_3-4(III)^5D_j$	66.55	$4^5D_3-n^5P_1$
51.78	$4^5D_4-4^5F_3$	34.19	$4^5D_3-5a^5P_2$	89.26	$4^5D_4-5(III)^5D_j$	60.71	$4^5D_2-n^5P_2$
44.51	$4^5D_3-4^5F_4$	30.25	$4^5D_3-5^5F_3$	86.99	$4^5D_1-3(III)^5D_j$	57.14	$4^5D_2-n^5P_1$
39.72	$4^5D_0-4^5F_1$	29.17	$4^5D_2-5a^5P_1$	79.27	$4^5D_2-4(III)^5D_j$	53.05	$4^5D_1-n^5P_2$
37.56	$4^5D_1-4^5F_2$	24.36	$4^5D_2-5a^5P_2$	71.64	$4^5D_2-5(III)^5D_j$	49.51	$4^5D_1-n^5P_1$
4289.73*	$4^7S_3-4^7P_2$	21.57	$4^5D_4-5^5F_5$	2780.69	$4^5D_4-nb^5P_3$	45.63	$4^5D_0-n^5P_1$
74.80*	$4^7S_3-4^7P_3$	20.67	$4^5D_1-5^5F_1$	69.91	$4^5D_3-nb^5P_2$	44.71	$4^5S_2-nc^5P_j$
54.34	$4^7S_3-4^7P_4$	18.83	$4^5D_2-5a^5P_2$	66.54	———	38.97	$4^5S_2-nc^5P_j$
3991.12	———	18.50	$4^5D_1-5a^5P_1$	64.35	$4^5D_2-nb^5P_2$	35.27	$4^5S_2-nc^5P_j$
83.91	———	15.20	$4^5D_0-5a^5F_1$	61.75	$4^5D_2-nb^5P_1$	2366.85†	$4^7S_3-5^7P_3$
41.59	$4^5D_4-4(I)^5D_j$	14.93	$4^5D_2-5^5F_2$	57.10	$4^5D_2-nb^5P_2$	65.16†	$4^7S_3-5^7P_3$
28.64	$4^5D_4-3(I)^5D_j$	14.77	$4^5D_1-5^5F_2$	52.87 48.29	$4^5D_1-nb^5P_1$ $4^5D_1-nb^5P_2$	64.74†	$4^7S_3-5^7P_4$

Bracketed lines are unresolved but both seem to be present.
* Observed by Hulburt in under-water spark, by Finger in under-water spark, Gieseler and Grotrian in vapor, by Zumstein in vapor.
† Observed by Zumstein in vapor.

Nickel. Finger[1] as well as Buffam and Ireton[4] has studied the under-water absorption spectrum of nickel. Angerer and Joos[23] have made observations on the line absorption of his element in the vapor phase. Table V shows the absorption lines observed in this investigation. The wave-lengths are those used by Bechert and Sommer[24] in their analysis of the nickel spectrum. It is to be noted that many new lines have been observed. These lines as well as those which have been previously observed are in agreement

[23] Angerer and Joos, Ann. d. Phys. **74**, 743 (1924).
[24] Bechert and Sommer, Ann. d. Phys. **77**, 351 and 537 (1925).

TABLE V

Absorption spectrum of nickel.

λ	Notes	λ	Notes	λ	Notes	λ	Notes	λ	Notes	λ	Notes
4466.54*	†	3571.87	1	3369.58	3	3057.65	1,2	2437.82*	†	2321.96	†
4202.33*	†	66.37	1,2	66.16	1	54.32	1,2	34.43	†	21.39	†
4074.89	†	61.75	†	65.77	1	50.83	1,2	24.03	†	20.03	†
10.14*	†	27.99	†	61.56	1	45.01	†	23.33	†	17.16	3
3973.55	†	24.54	1,2,3	22.32	1	37.94	1,2	21.33	†	13.98	3
72.16	†	23.44	†	20.26	1	31.87	1	19.31	†	12.34	2,3
3858.28	1	19.78	1	15.67	1,2	19.15	1	12.67	2	10.96	3
32.87	†	15.06	1,3	3282.70	†	12.01	1,2	10.68*	†	07.35	†
31.69	†	13.95	†	71.12	†	03.63	1,2	06.82*	†	06.45*	†
07.14	1	10.34	1	48.43	1	02.49	1,2	01.85	†	01.57	†
3793.60	†	07.70	†	43.06	1	2994.46	1	2396.39	2	00.77	†
92.33	†	00.85	1	34.66	1	92.60	1	94.50*	2	2298.23*	†
83.52	†	3492.97	1,2,3	32.95	1,2	84.13	1	93.12	†	96.54*	2
75.56	†	83.78	1	25.03	1	81.65	1	87.56	2	93.11	†
72.52	†	72.55	1	21.66	1	43.92	1	86.59	†	89.98	†
36.81	†	69.48	1	3197.12	1	14.01	1	84.40	†	88.39	†
22.48	†	61.66	1,2,3	95.58	†	07.46	†	76.02	†	87.32	†
3693.93	†	58.47	1,3	59.52	†	2865.51	†	69.22*	†	74.65	†
88.41	†	52.89	1,3	45.71	†	34.55	†	65.68	†	71.94	†
74.11	†	46.26	1,3	45.12		21.30	†	62.06	2	67.55	†
70.42	†	37.28	1	34.11	1,2	2798.65	†	60.64	†	61.41	†
64.09	†	33.57	1,3	29.31	†	46.75	†	58.87	†	59.45*	†
61.94	†	23.71	1	16.84*	†	2561.43	†	56.87	†	58.13	2
3649.63*	†	14.77	1,3	14.13	1	53.38	†	55.06	†	53.97*	†
34.94	†	13.94	1	05.47	1	47.42	†	48.74	†	53.55	2
24.73	†	13.48	1	01.88	1,2	24.22	†	47.53	3	51.47	†
19.39	1	09.48	†	01.56	1,4	2489.51	†	46.64	†	47.31*	2
12.73	1	3392.99	1,2	3099.12	1	84.04	†	45.55	†	13.29*	†
10.45	1	91.05	1	97.12	1	76.88	†	38.50	†	11.16*	2
09.31	1	85.34*	†	87.06*	1	72.24	†	37.49	3	06.80*	†
02.28	†	80.89	1	80.76	1,2	66.97	†	34.57*	2	01.55*	2
3597.70	1	80.58		75.85*	†	54.00	†	31.70	3	2191.04*	2
87.93	†	74.23	1	66.43*	†	50.48	†	2326.43*	†	84.70*	2
77.21	†	71.99	1	64.63	†	41.83	†	25.80	2,3	84.42*	†
										75.22*	2

Bracketed lines are unresolved but both seem to be present.
* Not classified by Bechert and Sommer. † New lines. 1. Finger in under-water spark. 2. Buffam and Ireton in under-water spark. 3. Angerer and Joos in vapor.

with the analysis of the spectrum as given by Bechert and Sommer. In addition to these classified lines a number of unclassified lines were found.

Cobalt. Table VI gives the results for cobalt together with the series classification as given by Catalan and Bechert.[25] The wave-lengths are

[25] Catalan and Bechert, ZS. f. Phys., **32**, 336 (1925).

those given by Dhein.[26] They are recorded only to two decimal places. Observations on the absorption spectrum of cobalt in under-water sparks have been previously made by Finger,[1] and also by Buffam and Ireton.[4] Both Angerer and Joos and Sur and Majumdar[27] have examined the absorption of this element in the vapor state. Except for minor departures the results of the present investigation confirm the earlier observations

TABLE VI

Absorption spectrum of cobalt.

λ	Notes	λ	Notes	λ	Notes	λ	Notes	λ	Notes	λ	Notes
4339.64*	†	05.37	†	33.04	1,2,4	62.20	†	2572.24*	2	65.04	3
20.37*	†	02.08	1,4	31.58	1	3061.83	1,4	67.33	†	2363.53*	2
03.24	†	3594.87	1,4	17.80	†	54.72	†	59.41*	2	58.21	†
4285.79	†	87.19	1,2	17.16	1	54.14		55.06	†	55.50	3
68.03	†	85.16	1,4	15.53	1	48.89	1,4	53.35	2	54.83*	4
52.30	†	84.80	4	14.74	†	44.01	1,2,3,4	53.00		53.43	3
34.00	†	79.03*	†	12.64	1,2,3,4	42.48	†	44.25	3,4	50.78*	2
4190.71	4	75.36	†	12.34	1,4	34.43	2,4	41.95*	2	46.58*	†
50.44	†	74.96		3409.18	1,4	17.55	2	38.78	†	46.18	3
21.33	1,2	69.38	†	05.12	1,2,3,4	13.60	†	35.93	3	45.05*	3
10.54	†	64.96	1,4	02.07*	†	05.77*	2	28.98	3,4	44.29	†
4092.40	†	60.90	1,4	3395.38	1,2,4	00.55	†	25.57*	2	35.98	3
76.13	4	58.78	†	90.80*	†	2989.60	1	21.40	3	29.15*	†
45.40	†	52.72	†	88.18	†	87.17	1,2,4	17.81	†	24.80*	†
20.90	†	50.60	†	85.23	1,4	29.52*	2	11.03	2	23.18	3
3997.91	2,4	42.98	†	83.92*	†	11.56	†	06.92*	†	21.26*	†
95.31	1,4	33.36	1,4	77.06*	†	2895.48*	†	00.51	2	19.27	†
87.12	†	29.82	1,3,4	70.33	2	86.45	†	2495.56	†	15.95*	†
65.24	†	29.04	1,4	67.11	†	50.96	2	76.64	†	13.71*	†
65.02		26.86	1,3,4	54.39	1,2,4	42.39*	4	76.43		11.65	2,3
57.94	†	23.44	1,4	46.94*	†	34.43*	†	73.92	†	09.03	†
52.92	†	21.74		34.15	1,4	33.93*	4	70.28*	†	04.22	†
35.97	†	21.57	1,4	33.39	†	20.00	†	67.71	†	2299.73*	†
33.92	2	20.09	1,4	25.24*	†	14.98	4	64.21*	†	96.25*	†
22.76	†	18.35	1,2,4	19.48*	†	11.53*	2	60.81	†	95.30*	3
3894.98	1,4	13.48	1,4	18.40*	†	2803.78	2	41.04*	†	93.05*	3
94.09	1	12.64	1,4	07.15*	†	2796.24	†	2439.03	3	2292.05*	†
3885.28	†	10.42	1,2,3,4	79.25*	†	74.96	†	36.77	3	90.35	†
84.61		09.84	1,4	65.35	†	64.19	†	32.20	3	88.84*	†
3873.96	1,4	06.32	1,3,4	64.84		52.07*	†	27.00*	†	87.86	3
73.12	1,4	02.62	1	49.99	4	45.11*	†	24.98	3,4	86.25*	2,3
45.47	1,2,4	02.28	1,2,3,4	47.18*	1,2,4	15.99*	†	23.63*	2	83.09*	†

[26] Dhein, ZS. wiss. Photo., **19**, 289 (1920).
[27] Sur and Majumdar, Phil. Mag. (7), **1**, 451 (1926).

TABLE VI (continued)

λ	Notes	λ	Notes	λ	Notes	λ	Notes	λ	Notes	λ	Notes
42.06	1,4	3496.69	1	43.84*	†	05.86*	†	22.57*	2	79.33*	†
41.46	†	95.69	1,4	37.03	†	2695.58	†	19.13*	†	76.75*	3
11.07	†	91.32	1,4	3186.35	†	94.68*	2	15.32	3	75.90*	3
08.11	†	90.74	4	74.91	†..	85.34	2	14.47	3	74.70*	3
01.23*	†	89.41	1,4	59.66	4	80.11*	†	12.88*	3	67.17*	2
3745.50	4	85.71*	†	58.77	4	75.99	2	11.65	3	65.82*	†
04.06	2	83.42	1,4	54.79*	2	63.53*	4	08.74*	†	62.63*	†
3693.48	†	76.37*	2	49.30	†	50.27	2,4	07.27	3,4	61.81*	†
93.12		74.02	1,3,4	47.06	4	48.65	2	02.12	3	37.25*	†
90.72*	†	65.80	1,2,3,4	39.94	2	46.42	†	2396.24*	†	34.86*	2
77.98	†	62.81	1,4	37.33	4	29.98*	2	91.99	3	29.12*	†
56.97	†	60.73	†	21.56	2,4	23.45	†	89.58*	†	27.84*	†
52.54	†	55.24	1	21.41		22.43	†	84.89	3	24.16*	2
47.66	4	53.51	1,2,3,4	03.99	†	22.25		83.45*	2	12.38*	2
31.34	1,4	49.44	1,3,4	86.78	†	2590.61*	†	80.52	3	07.89*	†
27.81	4	49.17	1,4	82.61	2	80.84*	2	78.62*	†	2204.9 *	†
24.96	4	43.65	1,4	72.35	1,4	78.93*	†	73.40*	†	2196.59*	†
18.01	†	42.92	1,2	71.95		74.36	2,4	71.76*	†	87.29*	†
15.39*	†	36.97*	†	64.38	2,4			71.40*	†	2181.12*	†

Bracketed lines not clearly resolved, though both seem to be present.
* Not classified by Catalan and Bechert. † New lines. 1. Finger in under-water spark. 2. Buffam and Ireton in under-water spark. 3. Angerer and Joos in vapor. 4. Sur and Majundar in vapor.

whether the absorption was obtained by means of the under-water spark or by means of the vapor of the metal. However, many lines not previously reported have been located and a more adequate confirmation of the series classification of Catalan and Bechert has thus been obtained. A number of new unclassified lines was observed and the presence of other unclassified lines confirmed.

DISCUSSION OF RESULTS

Indium and Gallium. The absorption lines found in the under-water spark spectra of indium and gallium confirm the results obtained from a study of the absorption by vapors of indium and gallium and in agreement with these results indicate that the normal state of the valence electron in both of these atoms is the *2p* state.

Manganese. The three prominent triplets characteristic of the absorption of manganese vapor have been found in the under-water spark spectrum of this element. The fact that all these triplets originate from the *1s* sextet level, shows that this term represents the normal state of the valence electron. A fourth triplet, ordinarily attributed to singly ionized manganese, has also been located.

Chromium. A large number of absorption lines not previously reported have been located in the under-water spark spectrum of chromium. These

lines give a rather complete verification of the arrangement of the energy levels in the chromium atom, above the ground $4S$ septet level. Not only were the three triplets arising from this term absorbed, but also almost all the classified multiplets whose final levels on emission, the quintet $4S$ and $4D$ terms, lie nearest the $4S$ septet level. The fact that the multiplets $4S$ originating from the $4S$ and $4D$ levels were absorbed, and those from other terms, such as the P-terms, were not absorbed, must be interpreted as showing the correctness of the assignment of the $4S$ and $4D$ levels as the next lowest to the $4^7 S$ level.

Nickel. In both nickel and cobalt more than a hundred lines were found which have not previously been observed in absorption. In each of these metals there is a group of terms relatively near the lowest or ground term. In nickel, according to the classification and notation of Bechert and Sommer the ground triplet term $f_4{}^1$ is followed successivley by the triplet terms $\bar{d}_3{}^1$, $\bar{d}_2{}^1$, $f_3{}^1$, $\bar{d}_1{}^1$ and $f_2{}^1$ and the singlet $\overline{D}_2{}^1$ which is separated by 0.4 volt from the term $f_4{}^1$. Since the singlet term $\overline{D}_2{}^2$ which immediately follows the $\overline{D}_2{}^1$ term is separated by 1.6 volts from the $f_4{}^1$ term, it would be expected that in the under-water spark the absorption lines would start from the f^1, $\bar{d}^1$, and $\overline{D}_2{}^1$ levels. The absorption lines as recorded in Table V start from these levels. Furthermore this table includes nearly all the lines of appreciable intensity which, according to the classification of Bechert and Sommer, originate from these levels. Hence these results seem to strongly confirm their assignment of terms and levels for nickel.

Cobalt. In cobalt above the ground term $f_5{}^1$ there are, in the notation of Bechert and Sommer, successively the quartet terms $f_4{}^1$, $f_3{}^1$, $f_2{}^1$, $f_5{}^2$, $f_4{}^2$, $f_3{}^2$ and $f_2{}^2$ and the doublet terms $F_4{}^1$ and $F_3{}^1$. The greatest separation to these terms from the ground level $f_5{}^1$ is about one volt but the $p_3{}^1$ term which is immediately above the $F_3{}^1$ term is separated by about 1.6 volts from the $f_5{}^1$ term. Hence the absorption lines to be expected on the basis of this classification should start from the f^1 or the F^1 levels. Because of the much greater separation of the p^1 levels from the f^1 levels, the lines which start from the p^1 levels are not to be expected. Almost every line of appreciable intensity Table VI corresponding to an initial level of $f_4{}^1$, $f_3{}^1$, $f_2{}^1$, $f_5{}^2$, $f_4{}^2$, $f_3{}^2$ and $f_2{}^2$ has actually been observed as an absorption line in the under-water spark. This fact gives a verification of the correctness of the term assignment of these lines and the arrangement of terms with respect to the ground level as given by Catlan and Bechert.

MENDENHALL LABORATORY,
OHIO STATE UNIVERSITY.

NOTE. Since the above was written a paper by Majumdar on the absorption spectrum of nickel appeared in Zeit. f. Physik, **39**, 562 (1926). On the basis of about one-half as many lines as are recorded in Table V, he concludes that there is not sufficient data available to determine the ground level of the nickel atom. At the Annual Meeting of the American Physical Society, Dec. 28–30, 1926, Meggers and Walters reported on the absorption spectra of iron, nickel and cobalt in under-water sparks. (Phys. Rev. (2) **29**, 358, 1927.)

STAGES IN THE EXCITATION OF THE SPECTRUM OF INDIUM

By John G. Frayne and Charles W. Jarvis

Abstract

The indium metal was vaporized at a temperature of 650°C in an iron cylindrical anode within a quartz tube. Electrons from an oxide-coated Pt filament passed through a helical grid into a force-free space where they collided with the atoms of indium vapor. The spectrum was viewed end-on through a transparent quartz window. At 3.3 volts the lines $2p_1-2s$ and $2p_2-2s$ appeared. At 4.2 volts the additional lines $2p_1-3d$ and $2p_2-3d$ appeared. At seven volts higher members of the series and several unclassified lines were present on the plates. At 13.2 volts the spectrum became very strong and the line 2306A appeared in addition to the recognized series lines. It is possible that the second arc spectrum was excited at this potential. The resonance lines were found to be less intense than the corresponding lines due to the metastable atoms.

Introduction

THE element indium is one of four members of the aluminum sub-group of Group III in the Periodic Table. The arc spectra of this group are characterised by series of well defined doublets and by the absence of the principal series found in the alkalis and alkali earths. Comparatively little research has been done on the spectra of this group. Mohler and Ruark[1] have studied the excitation by stages of the arc spectrum of thallium. Absorption spectra studies for thallium, indium and gallium have been made by Grotrian,[2] and also by Frayne and Smith.[3] Electrical resonance and ionization measurements on indium and gallium vapors have been made by Jarvis.[4] The indium used in this investigation was obtained from Mr. F. G. McCutcheon, Bartlesville, Oklahoma. Although some impurities were present it was found quite satisfactory at the temperatures employed.

Experimental Procedure

On account of the high boiling point of indium it is necessary to heat the metal to a temperature of 650–700°C before the vapor pressure is sufficient to show any spectral lines on a photographic plate when bombarded with fourteen volt electrons for a period of five or six hours. This necessitated the use of quartz or porcelain tubing. In Fig. 1, D is a transparent quartz tube with an optically plane quartz window E. A is a cylindrical iron anode to which the nickel grid helix B is welded. The open end of the quartz tube was fitted with an iron cap C which was sealed vacuum tight with de Khotinsky cement and water cooled. The filament leads were brought out through a glass tube H which was cemented to the metal cap C. The indium metal

[1] Mohler and Ruark, J.O.S.A. **7**, 819 (1923).
[2] Grotrian, Zeits. f. Physik, **12**, 218 (1922) and **18**, 169 (1923).
[3] Frayne and Smith, Phys. Rev. **27**, 23 (1926).
[4] Jarvis, Phys. Rev. **29**, 442 (1927).

was placed in the anode A and heat was applied by the electric furnace F. As the temperature was raised the indium metal tended to deposit on the quartz window and cloud it. This difficulty was overcome by placing the window in the hottest portion of the furnace. With this arrangement the tube could be operated for about ten days before any deposition was noticed.

The indium vapor proved to be very active chemically at 700°C. It combined with fine filaments of tungsten, molybdenum or platinum and with

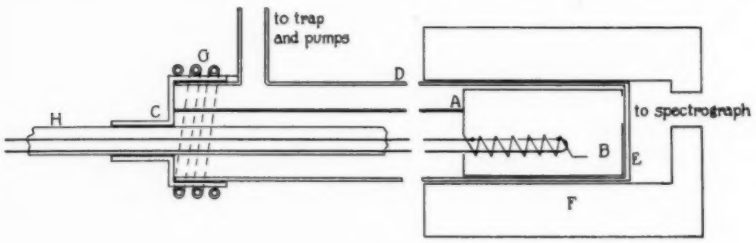

Fig. 1.

fine platinum strip. A 15 mil platinum oxide coated filament was found satisfactory, usually lasting about 120 hours. Electrons from this filament were accelerated through the nickel helix B into the force-free space between grid and anode where they collided with the atoms of the indium vapor. The resulting emission of spectral lines was viewed end-on through the opening in the anode. A Hilger E3 quartz spectograph was used throughout.

Experimental Results

The spectrum lines appearing at different anode voltages are given in Table I. It will be noticed that the first resonance line $2p_2-2s$ and the

Table I

Indium spectrum produced by electronic excitation.

Notation	3.3 v.	4.2 v.	6.9 v.	13.2 v.
$2p_1-2s$	4511.31 *A*	4511.31	4511.31	4511.31
$2p_2-2s$	4101.76	4101.76	4101.76	4101.76
$2p_1-3d$		3258.56	3258.56	3258.56
		3039.35	†3051.19	3051.19
$2p_2-3d$			3039.35	3039.35
			*2957.01	2957.01
$2p_1-3s$			2932.63	2932.63
			‡2858.30	2858.30
			*2836.91	2836.91
			*2775.35	2775.35
$2p_2-3s$			2753.88	2753.88
$2p_1-4d$				2710.26
$2p_1-4s$				2601.75
$2p_2-4d$				2560.15
$2p_1-5d$				2523.08
				‡*2306.07

* Listed as unclassified lines in the arc by Uhler and Tanch.
† Listed as an arc line by Kayser and Runge.
‡ Listed as a spark line by Exner and Haschek.

line of the metastable atom $2p_1-2s$ appear at the lowest voltage. The emission current was 0.3 m.a. and the time of exposure was 40 hours. At 4.2 volts the corresponding pair of lines resulting from transitions to the $3d$ level appeared in addition to the previous two lines. The current at this potential was about 0.6 m.a. and the exposure was for 24 hours. At 6.9 volts some higher members of the series appeared as well as several unclassified arc lines. Four of the latter are listed by Uhler and Tanch as arc lines. The line 3051A is given as a spark line by Exner and Haschek. The current at this potential was about 1.5 m.a. and the exposure lasted 14 hours. At 13.2 volts the arc became very brilliant the whole space between grid and anode being filled with a bluish-violet color. Up to this point the illumination was too weak to be observed by the eye. An exposure of three hours was found sufficient at this potential. A strong unclassified line 2306A appeared there. Several lines in the visible and near ultra-violet appeared here also, but they have been all traced to oxygen and other gaseous impurities.

Discussion

It was found that the intensity of the lines $2p_1-2s$ and $2p_1-3d$ were consistently stronger than $2p_2-2s$ and $2p_2-3d$. This was especially notable at the lower voltages. Mohler and Ruark[1] found a similar occurrence with thallium lines and attributed it to the fact that the resonance radiation was partially absorbed in the cool vapor above the furnace. Here, however, there was no column of cool vapor in the path of the light. Further, Frayne and Smith[3] have shown that at this temperature the $2p_1-2s$ is just as prominently absorbed as the $2p_2-2s$ line. This seems to indicate the return of atoms from the $2s$ or $3d$ levels to the $2p_1$ is more probable than to the $2p_2$ level. However, the work of Jarvis[4] by electrical method used for determination of resonance potentials indicated sharper and stronger current voltage breaks for the transition $2p_2-2s$. Since absorption spectra show that many indium atoms are in the metastable state at 700°C the valence electron may be ejected directly from the $2p_1$ directly to the $2s$ level. If all of these should return to the $2p_1$ in addition to others ejected to the $2s$ from the $2p_2$ state one can see that the $2p_1-2s$ line might be much more intense than the corresponding resonance line.

The entire arc spectrum should appear at 6.9 volts. It was found that several unclassified lines appeared at this potential. It is difficult to believe that these lines belong to the so-called second arc spectrum, being produced by multiple excitation. The small electron current, 1.4 m.a., makes this rather improbable. If these are bonafide arc lines the energy level diagram for indium must be much more complicated than one representing only the well known p, s and d levels. All attempts to prove these to be combination lines have been futile.

At 13.2 volts there was evidence of strong ionization. The electron current increased very rapidly at this stage and the glow in the tube was very noticeable. It is possible that two electrons were removed at this potential and the resulting spectrum might be considered as a second arc. Undoubtedly

many lines in these spectrum must lie in the far ultra-violet and, of course, could not be observed with an ordinary spectrograph. It is quite possible that the line 2306A may correspond to the 1855A line in the Aluminum spectrum.

ANTIOCH COLLEGE,
YELLOW SPRINGS, O. (J.G.F.)
OHIO WESLEYAN UNIVERSITY,
DELAWARE, O. (C.W.J.)
February 1, 1927.

SECONDARY RADIATION AND POLARIZATION OF RESONANCE RADIATION IN CADMIUM

By Walter A. MacNair

Secondary radiation in cadmium vapor containing mercury as an impurity.—Attention is called to the points of difference between the conditions under which the two types of optically excited spectra of mercury vapor appear, namely resonance radiation and fluorescence. In the present experiments it is noted that when a bulb containing cadmium with a slight impurity of mercury is illuminated by light of 2288A wave-length the secondary radiation contains the mercury line 2536.7A in addition to the cadmium lines 2288A and 3261A provided the metal is distilling. As soon as the vapor is stagnant, however, only the cadmium 2288A line appears. The suggestion is made that the phenomenon is due to the presence in the distilling vapor of unstable HgCd molecules. In such a molecule the Cd atom may absorb the 2288A radiation and subsequently in the breakdown of the molecule may excite the Hg atom by a collision of the second kind.

Polarization of the cadmium resonance, radiation in zero magnetic field.—The polarization of the cadmium resonance radiation (3261A) in zero magnetic field under certain conditions was found to be 35 percent. In order to explain this value by the kinetic theory, one must assign effective radii to the colliding atoms which are thirty times the radii effective in ordinary collisions.

THERE are two types of emissions from optically excited mercury vapor: the first appropriately termed "resonance radiation" by Professor R. W. Wood; the second, a bluish-green fluorescence. The names of Hartley, Wood, Steubing, Phillips, Van der Lingen and Wood, and Terenin[1] are associated with the study of the latter type. Van der Lingen and Wood concluded from one of these experiments, "However we interpret the results of the experiment, the fact is definitely established that only freshly formed mercury vapor is capable of exhibiting fluorescence." Professor Wood's explanation of the phenomenon, that is, that more diatomic molecules are evaporated into the vapor during active distillation than when the system is in equilibrium, has explained all the observations made up to the present time, although Pringsheim says that the explanation can hardly be brought into accord with thermodynamics.[2]

A similar phenomenon takes place in cadmium as shown by Terenin[3] who found that cadmium vapor at 150°C illuminated with radiation of 2288A emitted this radiation alone only when the vapor was in the stagnant condition and that when weak distillation of the cadmium was induced by *cooling* a spot on the tube the vapor emitted not only λ2288 but also λ3261. A source which is not good for exciting resonance radiation, that is, a source

[1] Hartley, Proc. Roy. Soc. **76,** 428 (1905); Wood, Phil. Mag. **18,** 240 (1909); Steubing, Phys. Zeits. **10,** 787 (1909); Phillips, Proc. Roy. Soc. **89,** 39 (1914); Van der Lingen and Wood, Astrophys. Jour. **54,** 149 (1921); Terenin, Zeits. f. Physik, **31,** 26 (1925).

[2] Pringsheim, Fluorescenz und Phosphorescenz, p. 81.

[3] Terenin, Reference 1.

in which the 2288 line is partially reversed, may be used to excite the distilling vapor in the above manner. The explanation given is similar to Professor R. W. Wood's explanation for the fluorescence in mercury vapor, which we have referred to. It is that diatomic molecules are evaporated from the surface of the metal during distillation in sufficient quantity to absorb an appreciable amount of radiation of 2288A wave-length. Some of these molecules then split apart after which one atom is in an excited state ready to emit λ3261 and the other one is in the normal state. These cadmium molecules are known to be very loosely bound and unstable which results in the fact that the molecular absorption bands surround the atomic absorption lines, thus permitting the light outside of the center of the 2288 line to be effective in the above experiment.

The fact that the 3261 line does not appear in the secondary radiation of stagnant vapor illuminated with light of 2288A wave-length under the conditions of the experiment mentioned above means, of course, that collisions of the second kind are too few to excite normal atoms to the $2P$ state. At 200°C the effect of such collisions is apparent.

During some observations preliminary to work on the polarization of resonance radiation in cadmium, another peculiarity of distilling vapor as

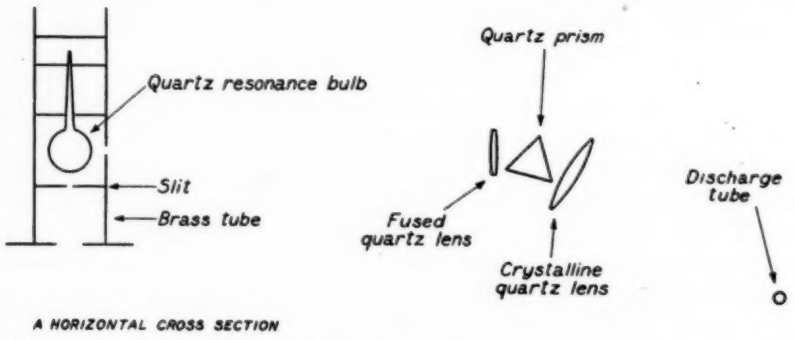

Fig. 1. Arrangement of apparatus.

contrasted with stagnant vapor was observed. Several variations of the disposition of apparatus described hereafter were actually used from time to time, but Fig. 1 shows an appropriate set-up which is the one that was finally employed. The source of light, which excited the secondary radiation in the bulb, consisted of a straight Pyrex discharge tube having large aluminum foil electrodes at the ends and a quartz capillary in the middle. Hydrogen was streamed through the tube at 0.04 mm mercury pressure, sweeping out the cadmium vapor which was distilled over from a side tube by placing the central portion of the tube in a furnace heated to about 200°C. The discharge tube was driven by a large 7000 volt transformer carrying about 15 amperes at 110 volts through the primary. Such a source of light is suitable for exciting resonance radiation. The quartz lenses focused the images of the discharge in the capillary on the brass tube, and with the aid of a fluorescing screen any desired wave length could be passed through the

opening in the side of the tube and into the quartz bulb. The secondary radiation in the vapor was observed at right angles to the primary beam and through the slit indicated, which served as the slit for the analyzing spectroscope. The temperature of the bulb and stem were read by thermometers placed in contact with the quartz, the former being kept thirty or forty degrees above the latter by heating the brass tube underneath the bulb with a Bunsen burner.

The quartz bulb containing the cadmium remained evacuated on the vacuum system several days before it was sealed off and used.

A characteristic observation results when the bulb containing a little cadmium having a slight impurity of mercury is heated to 170°C and the stem kept at 140°C. If the bulb is now illuminated with light of 2288A wavelength, the secondary radiation consists of 2288A, 3261A, and 2536 (Hg, $1S-2^3P_1$) as long as the metal is distilling from the bulb into the cooler stem, but just as soon as it has all left the bulb then only light of 2288A appears in the secondary radiation. The same thing has been observed with the bulb at 120°C and the stem somewhat cooler.

The appearance of the mercury line may be due to, (1) scattered λ2536 light from the source which contained mercury as an impurity, (2) collisions of the second kind between excited cadmium atoms or molecules and normal mercury atoms or molecules, (3) the evaporation from the metallic surface of HgCd molecules by a process outlined hereafter. Precautions were taken to prevent any light of 2536A entering the bulb.

The possibility that the appearance of the mercury line in the secondary resonance radiation can be explained by collisions seems to be excluded immediately because the pressure of the stagnant vapor in which the mercury line is not apparent is comparable with that of the distilling vapor in which it does appear. It must be stated, however, that since the bulb and stem were not in temperature equilibrium there may be some doubt as to the relative vapor pressures during and after distillation. Another possibility would occur if the Hg_2 molecules and the Cd_2 molecules evaporated from the surface have very large effective radii in collision.

If one assumes that loosely bound unstable molecules, made up of one mercury atom and one cadmium atom, are evaporated from the metal surface, the transfer of energy may be accounted for in the following manner. The molecule absorbs a quantum of energy of 2288A radiation and stores it by an electron jump in the cadmium atom; then in the breakdown of the molecule the disturbance in the mercury atom due to its partner, the excited cadmium atom, is comparable to a collision of the second kind which results in a normal cadmium atom and an excited mercury atom, plus a certain amount of kinetic energy.

There is independent evidence that HgCd molecules are formed when there is mercury present with the cadmium and that these molecules are capable of absorbing energy from the radiation of a cadmium arc. The absorption of pure and mercury contaminated cadmium vapor, under conditions which did not prevent distillation, has been studied by Wood and

Guthrie[4] who found decided differences in the absorption in the two cases. The most striking difference occurs exactly in the region in which we are most interested, namely, near 2288A. Pure cadmium vapor in a quartz bulb which is heated slowly, first reverses the 2288 line of a cadmium spark source in the center, the absorption line spreading with heating into a band symmetrical about the line. If mercury is present, however, the emission line of the source first reverses on the long wave length side and the absorption band spreads on the long wave length side with the rise in temperature of the bulb to 2307A before the 2288A line entirely disappears.

The mercury impurity was present in the cadmium in very small quantity and very intimately associated with it. The bulb had to be heated to 100°C before enough mercury vapor was present to show 2536A resonance radiation when excited by the unreversed 2536 line.

The quartz prism used as a dispersing piece between the source of light and resonance bulb, gave two images of the quartz capillary for each wavelength appearing in the discharge, one polarized horizontally and one vertically, separated sufficiently so that either one or the other could be focused on the opening in the side of the brass tube. Focusing the vertically polarized (electric vector vertical) 3261A beam so that it illuminated the stagnant vapor in the bulb which was at 252°C, the stem being at 212°C and photographing the cone of resonance radiation through a quartz Wollaston prism with pairs of varying relative exposure times until the weaker image in the longer exposure was of density equal to the stronger image in the shorter exposure it turned out that the resonance radiation was 35 percent polarized in a vertical direction when the bulb was in zero magnetic field. (The earth's field was neutralized to 0.02 gauss by a Hemhotz coil.) Under these conditions a spectroscopic analysis of the resonance radiation revealed, of course, secondary radiation of 3261A only.

It is generally assumed in accordance with Heisenberg's theory that mercury 2536 ($1S-2^3P_1$) resonance radiation excited in a bulb in zero magnetic field by 100 percent polarized light would be 100 percent polarized except for interatomic disturbances. If cadmium is in this case like mercury, and there is no reason to believe otherwise, then we must account for observing only 35 instead of 100 percent polarization on the basis of collisions where a collision is produced by a normal atom coming near enough to an excited atom to disturb its orientation so that the emitted light has a random plane of polarization.

From kinetic theory we may write the following formula[5]

$$\sigma^2 = 160 \times 10^{-23} (mT)^{1/2}/tp$$

where σ is the sum of the effective radii of the colliding atoms, t the average time between collisions, p the pressure in millimeters mercury, m the atomic weight, and T the absolute temperature. Under the conditions of our

[4] Wood and Guthrie, Astrophys. Jour. **29**, 211 (1909).

[5] See Datta, Zeits. f. Physik, **37**, 625 (1926); Schutz, Zeits. f. Physik, **34**, 260 (1925); Stuart, Zeits. f. Physik, **32**, 262 (1925).

experiment, p^6 is 5.5×10^{-4}, m is 112, and T is 525. If t were equal to the average life time of the excited atom, then 50 percent of the excited atoms would engage in a collision before returning to the normal state, but we observe that 65 percent have engaged in effective collisions so that the average time between collisions must be somewhat smaller that the life time of the excited state, not greatly, however, as an approximate calculation for this case gives the value of the former to be about 85 percent of the latter, so that for the purpose of our approximate calculation of σ we may take t to be 1×10^{-7}. This gives σ equal to 3×10^{-6} cms. The kinetic theory value of the radius of normal mercury atoms is 1.75×10^{-8} cms and the effective radius of 2^3P_1 mercury atoms when colliding with foreign gases is 5.9×10^{-8} cms[7] so that σ for mercury on kinetic theory is 7.6×10^{-8} cms. We would expect σ calculated for collisions between normal and 2^3P_1 cadmium to be slightly greater, or about 1×10^{-7} cms. Depolarization influences are felt thirty times farther away, however, as shown by the fact that to account for the present polarization observed, σ must be taken thirty times the above value.

Other cases of large effective radii have been observed. By comparing the percent of polarization of D_2 resonance radiation in sodium vapor at 10^{-6} mms pressure excited by polarized light with the percent predicted by the Heisenberg theory Datta[8] concludes that the effective radii of the colliding atoms are of the order of magnitude of 10^{-4} centimeters or about a thousand times the kinetic theory value.

By illuminating mercury vapor at various pressures in a magnetic field (fields of 2,000 to 18,000 gauss were used) with light of 2536A wave-length polarized with the electric vector parallel to the magnetic field and comparing the intensity of the part of the radiation polarized parallel to the magnetic field with the part polarized perpendicular to it. Schütz[9] calculates that normal mercury atoms and mercury atoms in the 2^3P_1 state collide 66 times as often as is given by a kinetic theory formula similar to the one given above using the data for the radii of normal and excited mercury atoms quoted above. If such a formula is to give the observed average time between collisions, we must consider the sum of the radii of the colliding atoms to be $(66)^{1/2}$ or 8 times the kinetic theory value.

On the other hand, if the effect of a foreign gas present in the resonance bulb is studied in the same manner, it turns out that the kinetic theory value for the time between collisions is nearly correct. From the work of Wood and Mohler[10] on the emission of both D lines by sodium vapor excited by one of them Schütz estimates that collisions, causing a transfer of energy, occur 50 times as often as one would expect on kinetic theory, or in other words, the sum of the effective radii of the colliding atoms is $(50)^{1/2}$ or 7 times the normal kinetic theory value.

[6] Edgerton, Phil. Mag. **33**, 33 (1917).
[7] Stuart, reference 5.
[8] Datta, reference 5.
[9] Schütz, reference 5.
[10] Wood and Mohler, Phil. Mag. **27**, 456 (1919).

The radii of atoms, which are effective in collisions, depends on what the result of the collision is to be. The largest effective radii are observed in cases which result in reorienting the atoms, that is in cases of depolarizing influences of neighboring atoms. Where there is a transfer of energy from one atom to another which is almost but not quite in resonance lesser effective radii are observed and cases of totally dissimilar atoms colliding result in still lesser effective radii.

The experimental work described here was carried on at The Johns Hopkins University during the spring of 1925, and I am indebted to Prof. R. W. Wood for his invaluable suggestions given from time to time. I was not satisfied with the interpretation of the results at that time so publication has been withheld until now.

January 10, 1927.

IONIZATION BY COLLISIONS OF THE SECOND KIND IN THE RARE GASES

By Gaylord P. Harnwell

Abstract

A positive ray apparatus was used to investigate the products of ionization by electron impact in mixtures of helium, neon, and argon. The variation with pressure of the ratio of the two types of positive ions present was investigated in detail for three cases. Case 1: A mixture of half helium and half neon was investigated up to 0.15 mm pressure. The ratio He^+/Ne^+ was found to decrease regularly between 0.03 mm and 0.15 mm. At 0.03 mm the mean free path is approximately equal to the dimensions of the apparatus. The suggested reaction is: $Ne+He^+ \rightarrow Ne^+ + He$. Case 2: A mixture of half neon and half argon was investigated throughout the same pressure range. The ratio Ne^+/A^+ decreased regularly between 0.05 mm and 0.15 mm, but this decrease was less rapid than that of the ratio in Case 1. The suggested reaction is: $A+Ne^+ \rightarrow A^+ + Ne$. Case 3: This mixture was half helium and half argon, and the pressure range was the same as in the first two cases. The ratio He^+/A^+ remained constant within the limits of experimental error. Case 3a: A mixture of 15 percent helium and 85 percent argon was also investigated as there were theoretical grounds for believing that the rate of variation of He^+/A^+ with pressure would be greater in such a mixture. In that case the ratio He^+/A^+ was found to decrease slightly. The suggested reaction is: $A+He^+ \rightarrow A^+ + He$.

The observed effects are best explained by a type of collision of the second kind which is equivalent to ionization by positive ions. To account for the results obtained an electron must be transferred from an atom to an ion at a certain fraction of the collisions between an atom and an ion of higher ionizing potential. The results obtained at low pressures corroborated the values for the probability of ionization in these gases obtained by K. T. Compton and C. C. Van Voorhis.

IN CONSIDERING certain experiments of Lind and Bardwell,[1] Professor K. T. Compton suggested the possibility of ionization by positive ions of high ionizing potential, probably as the result of collisions of the second kind. The present research was prompted by the belief that such a process might play an important rôle in many of the phenomena of ionization in gases and that it might be investigated by the modification of Dempster's positive ray apparatus used by H. D. Smyth[2] and Hogness and Lunn.[3] The rare gases were selected for the first experiments, as they are monatomic and have well known ionizing potentials, and consequently the results obtained from them would probably be the most easily interpreted. It was well known that the intensities of the peaks in a positive ray apparatus fell off rapidly at high pressures because of collisions of the ions with the atoms or molecules of the gas and subsequent deflection or neutralization. Hence it was thought that secondary effects of the type looked for would be expected to appear in the region just before the peaks were extinguished by

[1] Lind and Bardwell, Science, Dec. 25, 1925, Vol. LXII, page 593.
[2] H. D. Smyth, Phys. Rev., **25**, 452 (April, 1925).
[3] Hogness and Lunn, Phys. Rev., **26**, 786 (Dec., 1925).

the increased pressure. These effects would probably be intimately connected with the ionizing potentials of the two gases present. For they presumably represent the tenacity with which an electron is held in the atomic structure. If an ionized helium atom collided with a neutral neon atom it is conceivable that, because of the intensities of the fields involved, an electron would be transferred from the neon atom to the helium ion. The resulting bodies would then be a helium atom and a neon ion. The reverse of this process would not occur as the electron would then be originally attached to that atom which had the greater affinity for it. There would be no way of detecting any effects which might take place during the collision of an atom with an ion of its own kind. Hence the result which would be observed, in case collisions of the above kind took place, would be that the number of neon ions would be increased at the expense of the number of helium ions. The same reasoning would lead to the conclusion that argon ions would be produced at the expense of neon ions in mixtures of those two gases. Effects corresponding to the above were observed under various conditions, but the probability of the transfer occurring was not found to bear any simple relation to the ionizing potentials of the gases. While this investigation was in progress Hogness and Lunn[4] published the results of certain experiments they had conducted with argon and nitrous oxide during which they had incidentally observed effects of the same nature as those contained in this paper.

Apparatus and Procedure

The apparatus used is shown in Fig. 1. It is essentially the same as that used by Smyth[2] with only minor alterations. Chamber A, the high pressure region in which the ionization occured, was quite heavily shielded as was also the path between that and chamber B where the magnetic deflection took place. The shielding was thought necessary as rather large magnetic fields were used during some parts of the investigation and it was desired that the effect of changes in the field should be negligible except in chamber B. The distance between the slit, S_1, maintaining the pressure difference and the collimating slit, S_2, was made as small as was consistent with good evacuation from the upper outlet. The filament was placed very close to the first gauze, G_1, in order that the chance of a collision between an electron and an atom in that region might be reduced to a minimum. The filament itself was placed inside a tube the lower end of which supported G_1 and G_2. The tube was solid above G_1, but there were openings between G_1 and G_2. It was found convenient to have two gauzes during part of the work to investigate and interpret certain effects which were met. The filament was of tungsten. The width of S_1 was about 0.05 mm, that of S_2 was about five times as great. The gases to be used were mixed and stored in a system in which the pressure could be varied between convenient limits, and were then admitted to chamber A through capillary leaks. A McLeod gauge was situated as close to chamber A as possible. The evacuating system consisted of two single stage diffusion pumps backed by a double stage and an

[4] Hogness and Lunn, Phys. Rev., **28**, 849, abstract (1926).

oil pump. The large metal-to-glass seal was made by grinding the parts together and covering the joint with both DeKhotinsky and Picein cements. This joint proved quite satisfactory under the fluctuation in temperature to which it was subjected. It was found necessary to wind a cooling coil around the outside of chamber A which contained the filament.

As the apparatus could not be baked out it had to stand under vacuum for a day or two before the nitrogen, oxygen, water vapor, etc. adsorbed

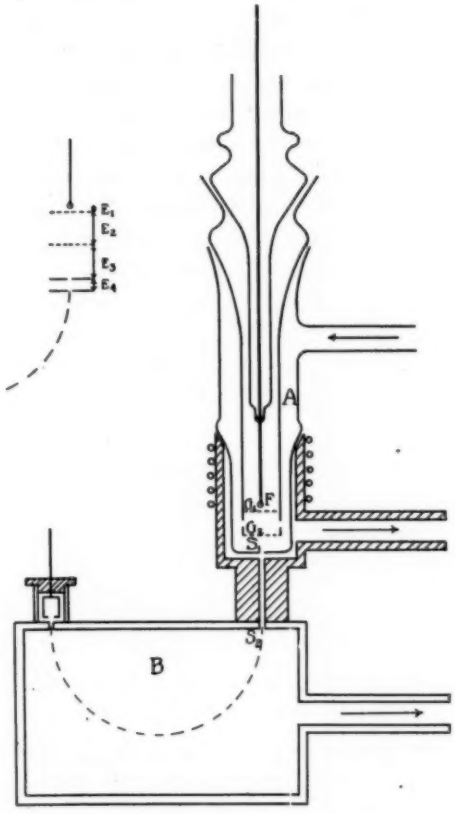

Fig. 1. Diagram of apparatus.

on the walls were reduced to a negligible quantity. Then after preliminary runs in hydrogen the behavior of pure helium was investigated under various conditions. At the high pressures used the amount of ionization was found to vary nearly linearly with the emission. In the final procedure the variable was the pressure and every change in pressure necessitated a slight change in the filament current in order to keep the emission constant. The fluctuation of the emission from one run to the next was very slight but sufficient to account for the greater part of the irregularity of the curves obtained. As E_1, the accelerating voltage for the electrons, was increased the ions began to appear very soon after the critical potential was passed, but the

amount of ionization did not rise very rapidly at first and the values of E_1 used during the work were in the neighborhood of twice the critical potentials. E_2 and E_3 the accelerating voltages for the positive ions were kept of the order of five volts in the final measurements as it was found that larger values introduced complicating effects which will be discussed later. The curves that follow are not strictly comparable as it was necessary to change the magnetic field for different gases and it was found, as will be mentioned later, that the ionization as measured by the electrometer was not independent of the magnetic field used.

The variation of the area under the peak with pressure was investigated and the results for helium, neon, and argon are given in Fig. 2. As would be expected the forms of the curves when the ordinates are multiplied by the proper constant are approximately the same. The constant probably depends on the value of E_1 used and the ionizing potential of the gas. The means of several runs were taken and the discrepancies could be accounted

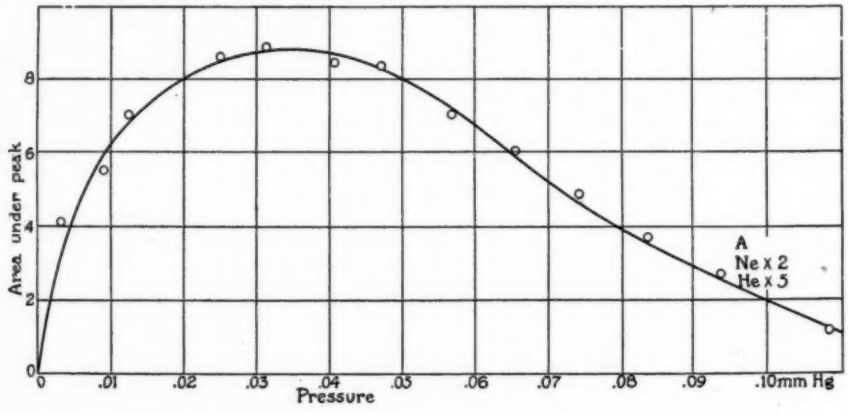

Fig. 2. Variation with pressure of the area under the peaks of positive ray analysis curves in A, He, and Ne.

for by the inevitable slight variations of voltages and filament emission. The abscissas are the pressures and the ordinates are measured in arbitrary units. A maximum of ionization occurs when the pressure is between three and four hundredths of a millimeter. The decrease in ionization after that point is presumably due to collisions with gas atoms resulting in deflection or neutralization, and it is therefore in that region that any secondary effects should be expected.

Several procedures were tried, such as taking runs at constant total pressure with varying mixtures of helium and neon, or with a constant partial pressure of one of the gases and varying the partial pressure of the other. These experiments showed in a qualitative way that some such an effect as the one looked for was actually taking place but they did not lend themselves to accuracy of measurement or ease of interpretation. The procedure finally adopted, as least equivocal and best adapted to the particular investigation, was to admit the gases in known and nearly equal proportions

and to vary the total pressure. The secondary effects would not be expected to occur below three hundredths of a millimeter pressure and should come more into evidence as higher pressures were reached. In this method the only variable was the pressure and it was susceptible of quite accurate measurement.

RESULTS

The first attempts were made using potentials for E_2 and E_3 in the neighborhood of fifteen or twenty volts. It was found that under these conditions the effects were complicated by having all the peaks double. The duality of the peaks was found to vary only with the potentials E_2 and E_3. If these potentials were large the peaks were widely separated and as they were decreased the peaks became indistinguishable when E_2 plus E_3 was in the neighborhood of twenty volts. If E_3 was small and its direction reversed the extraneous peak was very much reduced. This and other evidence of a similar nature pointed to the theory that the second peak was produced by photoelectrons emitted from G_2 and S_1 and accelerated upward towards G_1. This effect was eliminated by reducing E_2 and E_3 till their sum was well below the ionizing potential of any gas used. This still left the currents measured by the electrometer of a convenient order of magnitude. Other sources of slight error or irregularity were investigated and their effects reduced as much as possible.

The gases were thoroughly mixed in the reservoir by a method of contraction and expansion and also allowed to stand for some time after mixing before the runs were taken. Furthermore the possibility of a change in the ratio of the gases on passing through the capillary leaks into chamber A was considered. That is, it was thought that there might be a differential effect between the capillary method of pressure limitation and the slit method at S_1 in favor of one of the gases. This effect was investigated and found not to exist within the limits of experimental error. Any error due to minor irregularities in the mixture was greatly reduced by taking the mean of a series of observations. All the results were converted into the form of ratios and hence were independent of the fact that there is probably not an exact correlation between the area under the peaks and the number of ions present. However, the variation in size and shape of a peak with the magnetic field as a source of error will have to be mentioned again in the case of helium and argon.

By far the largest and most serious possibility of error is due to stray ionization present in chamber B. The electrometer was adjusted so that its natural drift when the filament was not glowing was extremely small. But as soon as ions were produced in A the drift increased. It is very probable that a small fraction of the ions entering B instead of continuing in a circular path are scattered from the beam. Some of these ions enter the Faraday cylinder and cause a deflection of the electrometer. This effect is more marked at low values of E_4. And the possibility of error in that region was further enhanced by slight traces of N_2 and H_2O which could not be completely

eliminated. For equal areas of peaks the height as measured by the current to the electrometer varies to a first approximation as E_4, so that the total error due to these effects became more serious with a gas of high atomic weight such as argon. Or more particularly when the discrepancy between the atomic weights of the two gases used was large. For if the atomic weights were not widely different the difficulty could be overcome by increasing the magnetic field and hence the corresponding value of E_4 for the peaks which would decrease the error due to scattered ionization. This will have to be mentioned again in the case of argon and helium.

The first gases used were helium and neon. The result in the case of a mixture of fifty percent of each (by volume) is shown in Fig. 3. The pressures plotted are the total pressures, the partial pressure of each gas being half of

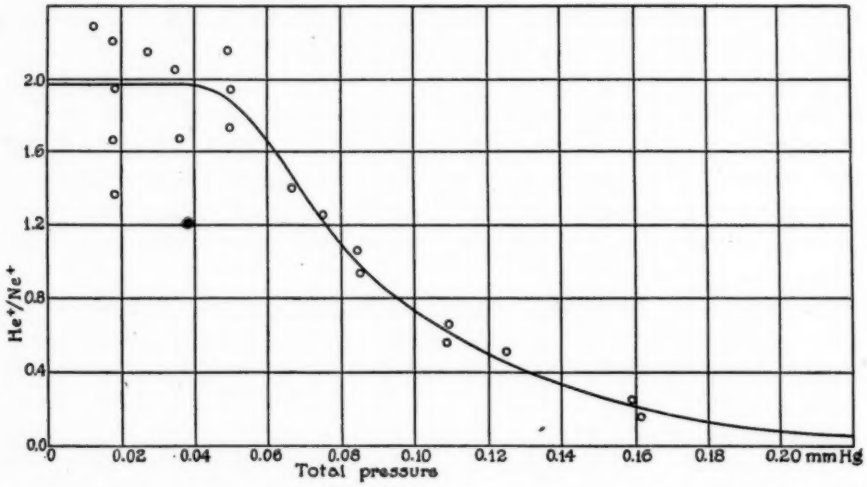

Fig. 3. Ratio of He^+ to Ne^+ for various pressures of a 50 percent mixture of He and Ne.

the pressure shown. The ordinates represent the ratio of the helium ions to the neon ions, as obtained by taking the areas under the peaks representing the two gases. E_1 was fifty volts and E_2 and E_3 were five volts apiece. The emission from the filament was maintained as nearly as possible at one milliampere. In this case the most convenient magnetic field to use with the available limits for E_4 was about 1700 gauss. In the region of pressure below five hundredths of a millimeter the ratio fluctuated rather widely. There seems to be no really adequate explanation for this. The most probable cause is that more difficulty was experienced in keeping the filament emission at a constant value in this region. The mean, however, remained practically constant. After the pressure passed five hundredths of a millimeter, approximately, the ratio dropped showing a predominance of neon ions. This is about the pressure judging from Fig. 2 at which any secondary effects should become noticeable. This is also the point at which the effect should occur from a more direct point of view. The distance between G_1 and S_1 was approximately two centimeters, and the pressure at which effects due to

collisions should become evident would be that at which the mean free path was of about this length. This should occur in these gases at about five hundredths of a millimeter. From this point the curve drops in a fairly regular fashion, and apparently approaches a lower value asymptotically. In the case of helium and neon the final value, if one exists, seems to be a very low one. It is probably closely related to the process of exchange of an electron from an atom to an ion outlined above. The difference between the original and final value of the ratio may even be a measure of the probability of the transfer occurring. It was not possible to carry these observations much above fifteen hundredths of a millimeter as the peaks had become very small by the time that pressure was reached. Also, for the same reason, the observations were less accurate as the drift of the electrometer due to scattered ionization had become a very appreciable fraction of the area of the peak. That was allowed for but it could not be done with great accuracy.

The next mixture used was that of neon and argon. In some ways this was a more favorable mixture to work with in a positive ray apparatus than

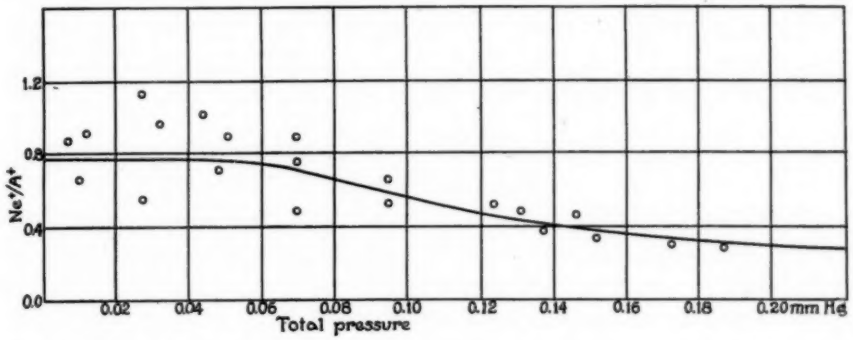

Fig. 4. Ratio of Ne^+ to A^+ for various pressures of a 50 percent mixture of Ne and A.

the previous one for the ratio of the atomic weights is 5:9 instead of 1:5. The reason that the value of this ratio effects the accuracy was mentioned above. Also the ionizing potentials are slightly lower, and the difference between them is about twice that in the previous case. The results for this mixture are shown in Fig. 4. As before the abscissas represent the total pressures and the mixture contained equal proportions of each gas. The ordinates are again the ratios of the areas under the peaks, but they are not strictly comparable to the ordinates in Fig. 3 for the magnetic field was about 3000 gauss in this case and the ionization as measured by the electrometer was not independent of the magnetic field. This curve shows the general characteristics of Fig. 3. The values of the ratio at lower pressures fluctuate rather widely as before. The most distinctive feature is that the change in the ratio of the ions with pressure is very much less than in the case of helium and neon. It also looks as if the slope approaches zero at higher pressures, but the evidence for this is not very conclusive.

The third mixture investigated was that composed of half helium and half argon. The conditions under which these observations were taken were as nearly as possible those of the previous runs. E_1 was fifty volts, E_2 and E_3 were five volts apiece, and the emission was kept at one milliampere. The magnetic field first used was about 2000 gauss. Approximately the same range of pressures was covered and with the same procedure, but within the limits of error no departure from the original value of the ratio of helium to argon was observed. However, the results were less convincing than in the two previous cases for the fluctuation in the actual areas of the peaks at constant pressure was considerably larger. This was due to the particular gases used for they were the least satisfactory ones to investigate by this method, the ratio of the atomic weights in this case being 1:9. Hence the argon appeared at a comparatively low value of E_4 and had a broad low peak much less susceptible to accurate measurement than the helium one. The particular difficulty, of course, was due to the electrometer drift caused by the scattered ionization in the argon region. Attempts were made to find a more satisfactory method of procedure. The most promising one was to investigate the behavior of one of the peaks, in this case the argon one, with

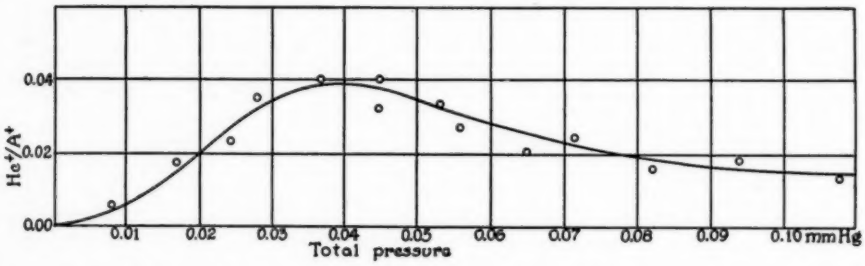

Fig. 5. Ratio of He^+ to A^+ for various pressures of a mixture of 15 percent He−85 percent A.

variation in the magnetic field and consequent variation in E_4 at different pressures. This was done and curves were obtained relating the peak area to the value of E_4 at which it was obtained. These were found to depend slightly on the pressure. With these data the two peaks of helium and argon could be measured at different magnetic fields such that the E_4 values at which they appeared were of the same order. By this means the area under the argon peak could be measured more accurately and its value extrapolated back to the value which it would have if measured at the same magnetic field as that used in obtaining the helium peak. This method yielded more consistent results and was presumably of greater accuracy. However, no change in the ratio of the peaks, within the limits of error, could be observed as the pressure was varied.

From simple kinetic theory considerations it can be seen that if this effect takes place as assumed, the rate of variation of the ratios: $He^+/(He^+ + A^+)$ and $A^+/(He^+ + A^+)$, with pressure should be greatest when the ratio of helium to argon is small. Acting on these considerations a mixture of 15% helium and 85% argon was investigated. The conditions

were almost the same as in the other experiments and the results are shown in Fig. 5. The ratio increases to a maximum at about .03 mm as would be expected from consideration of the partial pressure of the gases. After that point the ratio decreases slightly tending to show that the argon ions are being increased at the expense of the helium ions. Further evidence that this effect is taking place is given by the shapes and positions of the peaks. As the pressure increases beyond about .03 mm the He peak decreases in area but remains of the same shape and in approximately the same place. The argon peak decreases slightly but also broadens out and extends to higher values of E_4 showing that the region of production of argon ions is moving from G_1 toward S_1. The evidence thus indicates that the process observed in the other mixtures occurs in a mixture of helium and argon though it is much less probable.

Discussion

The outstanding result of these experiments is that this type of ionization by positive ions apparently does occur. Further experiments have been made with mixtures of the rare gases and gases whose molecules are diatomic. These results will form the subject of a later paper, but they tend to confirm the evidence contained in this one. If this effect occurs at a certain fraction of the collisions in any mixture of ionized gases it should have an important bearing on almost all discharge tube phenomena. A rough estimate of the probability of this electron transfer can be made from the slopes of the curves but the data are as yet insufficient to justify the publication of a numerical value.

The shapes of the curves in Figs. 3 and 4 further suggest that the probability of the transfer of an electron from an atom to an ion is not connected in a simple way with the electron affinities of the two gases involved. In fact, it even seems that though a difference in ionizing potential is necessary to cause such a transfer, yet the smaller this difference the more likely such a transfer is to occur. For the difference in ionizing potential between neon and argon is twice that between helium and neon. If this is so, and it is a result consistent with those of other experiments on collisions of the second kind, it accounts for the smallness of the effect in the case of helium and argon. For in this case the difference in ionizing potential is three times that in the case of helium and neon. These remarks apparently also apply to diatomic gases.

It should also be mentioned that the possibility of explaining the observed effect on the basis of a limiting speed for electrons in a mixed gas was considered. At sufficiently high pressures inelastic impacts would prevent the electrons from gaining sufficient energy to ionize the gas with the higher ionizing potential. However, such a situation could only exist when the length of the electron mean free path was of the order of the distance from the filament to G_1, which from the constants of the apparatus would occur at a pressure of about 1.5 mm. This is very much higher than any pressure used.

Finally it might be mentioned that the mean values obtained for these ratios below three hundredths of a millimeter are in fairly good agreement with the values obtained by Compton and Van Voorhis[8] for the probability of ionization in these gases. It was mentioned above that the area under the peak is probably not an accurate measure of the ionization in chamber A and also that the peak area varied with the values of magnetic field and E_4 used to obtain it. The points on the curves given here all represent runs in which the magnetic field was kept constant and the value of E_4 was varied. The behavior of peak area with magnetic field was investigated and from these results Figs. 3 and 4 can be replotted in such a way that the points represent runs in which E_4 is kept constant and the magnetic field varied. If this is done the shapes of the curves remain the same but the actual values of the ordinates are slightly different. And the ratios at low pressures when these ordinates are used are in quite good agreement with the same ratios calculated from the Compton and Van Voorhis results at the appropriate E_1.

My thanks are particularly due to Professor K. T. Compton and Professor H. D. Smyth for the suggestion of the present investigation and for their invaluable assistance and helpful interpretations during the work.

PALMER PHYSICAL LABORATORY
PRINCETON, NEW JERSEY
February 5, 1927

[8] Compton and Van Voorhis, Phys. Rev., **27**, 724 (June, 1926).

CHANGES IN THE PHOTO-ELECTRIC THRESHOLD OF MERCURY

By Hugh K. Dunn

Abstract

Photo-electric threshold for the clean surface.—C. B. Kazda has found the photo-electric threshold of a mercury surface cleansed of impurities by means of a constant overflow. In the present work his value of 2735A for the threshold of clean mercury is checked.

Changes in photo-electric threshold of Hg. that take place in a high vacuum.—When the surface flow is allowed to stop in a high vacuum, some impurity attacks the surface, quickly raising the threshold to 2850A. If liquid air is not used, this impurity is present in larger amounts and attacks the running surface. Indications are that a surface film is formed and maintained in spite of the flow when liquid air is not used, or requires two hours or more for removal if liquid air is used. This impurity can not be one of the gases with extremely low melting points. It is not water, but may be a component of the stopcock grease. When the surface is left standing several days in a high vacuum, its threshold falls to 2680A. If liquid air is not used, the standing surface has a limit of 2560A. All of these values are closely reproducible.

Indirect effect of hydrogen on the photo-electric threshold of Hg.—Pure hydrogen in contact with the surface does not change the photo-electric behavior. When the mercury is condensed in the presence of hydrogen, some of the gas is dissolved in the metal. This does not change the characteristic threshold of the mercury. It does, however, have the effect of greatly impeding the action of other impurities that form on the surface. This is indicated by the fact that over two hours is required for the change from the threshold of 2735A for the clean surface to the maximum of 2580A, as compared with 13 minutes for this change when hydrogen is not present.

THE photo-electric threshold for mercury has been found by Kazda[1] at 2735A. He was able to eliminate all effects of impurities by making his measurements on a flowing surface. This was probably the first time that a clean surface of metal had been used in photo-electric experiments, with any degree of certainty, and it was thus possible for him to demonstrate that a metal does possess a definitely characteristic threshold. At the same time, the clean surface offers the best possible starting point for an investigation of the effect of impurities on the threshold. It was for the latter purpose that the work reported in the present paper was undertaken.

Apparatus and Method

The experimental arrangement was, in the main, just as it was used by Kazda. The reader is referred to his paper for a diagram of the apparatus and a more detailed account of the experimental method. Briefly, the surface flow was realized by operating a mercury still and allowing the condensed mercury to overflow from a cup inside the photo-electric cell. The source of light was a quartz mercury arc, and a monochromatic illuminator was

[1] C. B. Kazda, Phys. Rev. **26**, 643 (1925).

arranged to direct light of any desired wave-length onto the mercury surface. The relative intensities of the lines of the arc were measured by means of a delicate thermopile, in vacuum. The photo-electric effect of any given wave-length was measured by a quadrant electrometer by the usual rate of deflection method. The photo-electric effect per unit intensity was then plotted as a function of the wave-length, and the intercept with the wave-length axis gave the threshold, with an uncertainty of not more than ± 10A. When it was desired to follow rapid changes in the sensitivity the rate of deflection method was too slow. In such cases a constant deflection method was used, the quadrants connected to the photo-cell being shunted to the ground by a radioactive leak.

The Threshold for the Flowing Surface

The value found by Kazda for the long wave-length limit of the flowing surface of mercury was 2735A. In more than a dozen determinations in the present work, this limit was always found between 2735A and 2750A. It

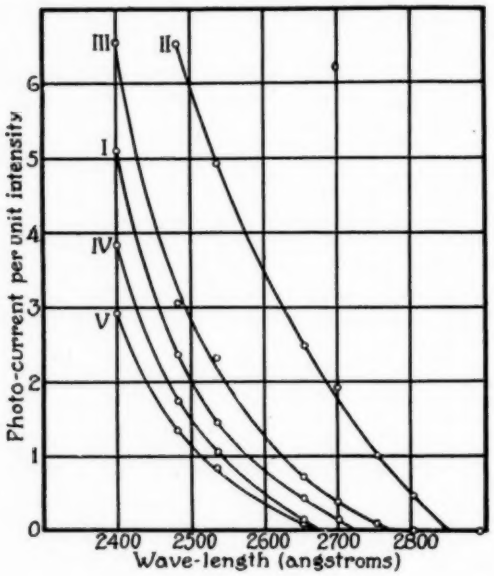

Fig. 1. Change of threshold of mercury. I. Curve for flowing surface. II. 13 minutes after turning off still. III. 18 hours after turning off still. IV. 66 hours after turning off still. V. 114 hours after turning off still.

must be noted too, that the higher values were obtained under less favorable conditions, i. e. less prolonged pumping and running of the still since the last contamination of the surface. A curve for the clean surface is shown at I, Fig. 1.

Stationary Surface in High Vacuum

Curve I, Fig. 3, shows the changes that take place in the sensitivity to the line 2653A, when the clean surface is exposed to a vacuum of the order

of 10^{-6} mm of mercury. Before this experiment was started the surface had been flowing for some time and showed the normal threshold of 2735A. The sensitivity was constant. At the time marked zero the still was turned off. The surface flow immediately slowed down, and in about ten minutes stopped altogether. As may be seen from the curve, the sensitivity to 2653A rose to a maximum of about five times that when running, about 13 minutes being required for the rise. The sensitivity then began to decrease, rather rapidly for about 40 minutes, then more slowly. This slow fall continued over several days.

Fig. 1 shows the threshold curves for the changing surface. Curve I is for the flowing surface, and gives 2735A for the threshold. Curve II is for the highest point reached after stopping the flow, i. e. about 13 minutes after turning off the still. The limit given is 2850A. Curve III was taken after 18 hours of standing, the limit having now fallen to 2770A. Curve IV was taken after 66 hours, and V after 114 hours. Both show a threshold of about 2680A, indicating that a constant value has been reached. It is to be noted that the threshold first rises some 115A above that for clean mercury, but eventually drops to 55A below that value. It should be explained that curve II was not taken all in one run, as were the others, for the reason that the surface does not remain in the most sensitive condition long enough for a threshold curve to be taken. It was obtained by successively running curves like I, Fig. 3, for the different lines of the arc, the highest point of each being used for plotting the point of II, Fig. 1, for that wave-length.

From a study of these results it would seem that there are at least two stages to the process of contamination of the surface. This might be attributed to two different impurities, one acting very quickly and raising the threshold, the other lowering it, but acting much more slowly. It is more likely that one agent is responsible for both phenomena, a single layer of molecules assisting the release of electrons, but greater thicknesses tending to stop the slower electrons and thus lower the threshold. This is in accord with the results of Becker[2] on the thermionic work function of platinum covered with caesium.

Contamination by Removal of Liquid Air

Marked changes in the long wave-length limit and sensitivity took place when the liquid air was removed from the trap connected with the apparatus. When this was done with a surface that had been standing for some time in a high vacuum, a drop in the threshold occurred. For example, the surface had been standing in a high vacuum for 46 hours, and showed a threshold of 2785A. With the pumps running continuously, the liquid air was removed. An immediate drop in the sensitivity to the 2653 line was noticed, and after two hours time it had fallen to zero. A threshold curve then showed the limit to be 2570A. This curve is shown at I, Fig. 2. After 20 hours curve II was taken. The limit had remained practically the same, falling perhaps to 2560A. The sensitivity, however, especially for $\lambda = 2400$A,

[2] J. A. Becker, Phys. Rev. **28**, 341 (1926).

had decreased considerably. This value of 2560A was obtained repeatedly, and may then be taken as characteristic of standing mercury contaminated by something that is released when the liquid air is removed. After curve II was taken, the liquid air was replaced, and after 22 hours the threshold was found to have risen to 2600A, the surface not having been disturbed meanwhile. This was repeated on another occasion, the limit 2600A being observed after the liquid air had been replaced for 56 hours.

On one occasion a slight rise in sensitivity was first observed when the liquid air was removed. The surface had been standing for only a few hours, and had the limit 2830A. The deflection for $\lambda = 2653$A was 253 mm. When

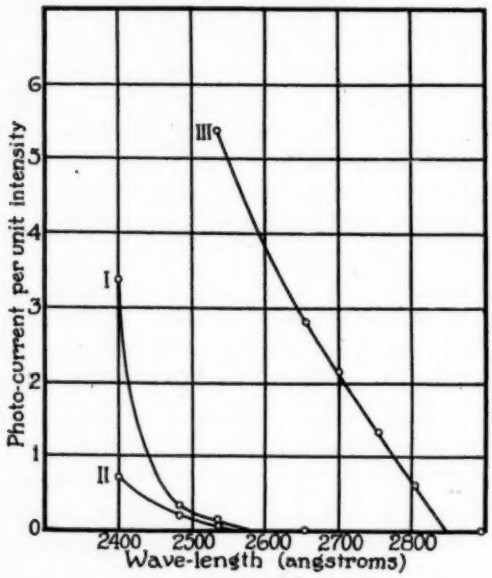

Fig. 2. Effect of removal of liquid air on the threshold. I and II. Curves for standing surface. III. Curve for flowing surface.

the liquid air was removed it rose in six minutes to 272 mm, then proceeded to drop in the usual manner. The threshold reached the value 2560A in two hours time.

When the liquid air was removed while the surface was running, nothing happened until the trap reached such a temperature that the frost began to disappear from its outside. Then, however, a sharp rise in sensitivity was noticed, while the threshold rose from the usual 2735A to the value 2850A. The curve is shown at III, Fig. 2. The rate of flow was increased until the surface was too turbulent to permit consistent results, but no change in this value was obtained. After the liquid air was replaced, several hours of pumping and running the still were required to bring the threshold back to normal. Repetition of the experiment gave identical results.

It thus appears that there is some impurity that can attack even the flowing surface if present in large enough concentrations. Furthermore, it seems probable that this is the same impurity that causes the highest

sensitivity of the surface standing in a high vacuum, since the same threshold, 2850A, was observed in both cases. When liquid air is used, the concentration of this impurity is not high enough to permit its attacking the flowing surface.

While the highest values reached by the threshold are identical, there is a difference in the lowest values reached by the standing surface, with and without liquid air. In the former case, there is a definite tendency to stop at 2680A, while in the latter case the limit falls to 2560A.

The impurity responsible for the threshold of 2850A would seem to be something whose vapor pressure increases rapidly in the neighborhood of 0°C. To test whether or not it is water vapor, a side tube containing a little water was sealed to the apparatus between the liquid air trap and the photocell, and immersed in liquid air. Liquid air was also kept on the regular trap. The apparatus was exhausted and the mercury surface brought to its normal running behavior. The 2653 line gave a deflection of 178 mm. The liquid air around the water was then replaced by brine at −20°C. The deflection began to fall very slowly, reaching 125 mm after 2½ hours. The brine was then removed, and the fall was more rapid, the deflection going to 92 mm in about 14 minutes. The liquid air was replaced, and the deflection rose in 9 minutes to 174 mm, close to its former value. At no point was any rise in sensitivity noted due to the release of the water, in spite of the fact that the brine was used to insure a very slow release at first. This result is not necessarily inconsistent with that of Kazda, who found that small amounts of water vapor cause a rise in the threshold of a standing mercury surface, for here the experiment was made with a flowing surface.

Since stopcocks were used as a part of the apparatus, it is evident that vapor from the stopcock grease must have been condensed in the liquid air trap. A side tube containing a small quantity of the grease was sealed to the apparatus, and treated in the same manner as the water had been (except that brine was not used). With pumps running and surface flowing, the liquid air was removed from the grease, while that on the regular trap was kept in position. This time the rise in sensitivity and threshold was observed, the latter reaching and holding the value 2850A quite exactly. While these tests are not entirely conclusive, it is very probable that some component of the grease is responsible for many of the changes observed.

Hydrogen in Contact with the Surface

Extensive tests were made with hydrogen in contact with the mercury surface. The hydrogen was purified, and admitted to the apparatus at pressures ranging from 10^{-4} to 10^{-1} mm, and tests were made both with the standing surface and with the surface flowing at various rates. Observations were also made of the changes taking place when the surface flow was allowed to stop. In all cases the behavior was exactly as when the hydrogen was not present, with the exception that when the pressure exceeded 10^{-3} mm a slight decrease in the photo-current was noticed. This was undoubtedly a space, not a surface, effect, for it was roughly proportional to the pressure, and the same effect was observed when air was used instead of hydrogen.

We must conclude that pure hydrogen does not modify the surface in a way that affects the photo-electric behavior.

Hydrogen Present in the Still

Suhrmann[3] has proposed a theory that in an electron emission of any kind from a metal, a gas dissolved in the metal has the effect of increasing the emission, while an adsorbed layer of gas on the surface decreases the emission. An experiment was devised to test this theory, and, while it failed to confirm the theory, an interesting effect was discovered.

The apparatus had been constructed in such a manner that the still was connected with the photo-cell only by two small tubes. One of these contained the condensed mercury flowing to the cell, the other contained the overflow from the cell, running back to the bottom of the still. Since both tubes were full of mercury, a pressure of several centimeters could be

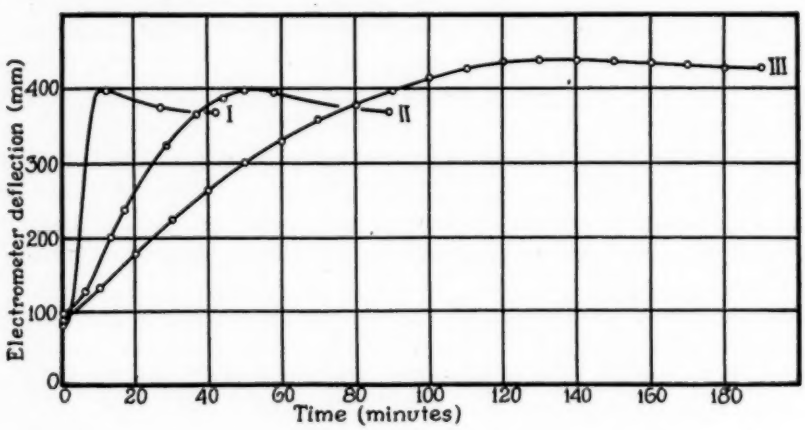

Fig. 3. Rise of sensitivity after stopping surface flow. I. Curve taken in high vacuum. II and III. Taken with hydrogen in the still.

maintained in the still without affecting the pressure in the cell. The two parts of the apparatus were connected to the same pumps, but could be separately closed off by means of large mercury-sealed stopcocks. A separate liquid air trap was provided for each branch. It was then possible to admit hydrogen to the still, while a high vacuum was maintained in the photo-cell.

With the still running, hydrogen was admitted to it, to a pressure of 8 mm. It was thought probable that some of the hydrogen would dissolve in the condensing mercury, and flow with it through the small tube to the photo-cell. An increase in emission would then occur if Suhrmann were right. No such increase in emission was observed, although the electrometer deflection was carefully watched for more than two hours, during which time the small tube leading to the cell must have emptied many times. No change in the sensitivity or threshold of the flowing surface occurred.

[3] R. Suhrmann, Zeits. f. Tech. Physik, **4**, 304 (1923).

When, however, the still was turned off and the surface flow allowed to stop, *the time required for the rise to maximum sensitivity was 49 minutes.* Two days previous, this time had been 12 minutes. In the year preceding and the two months following the experiment described here, this time of rise was observed under high vacuum conditions some 27 times, and always found to lie between 11 and 20 minutes. The 20-minute rise had been observed on only one occasion, the most common value being 13 minutes. The 49-minute rise was then a radical departure in behavior. It is shown in curve II, Fig. 3, where it may be compared with I, taken without hydrogen present. It is noticed that the highest sensitivity is practically the name, the only difference being the introduction of a time factor.

Curve I, Fig. 4, is the threshold curve for the flowing surface, either with or without hydrogen present in the still. Curve II was taken when the highest

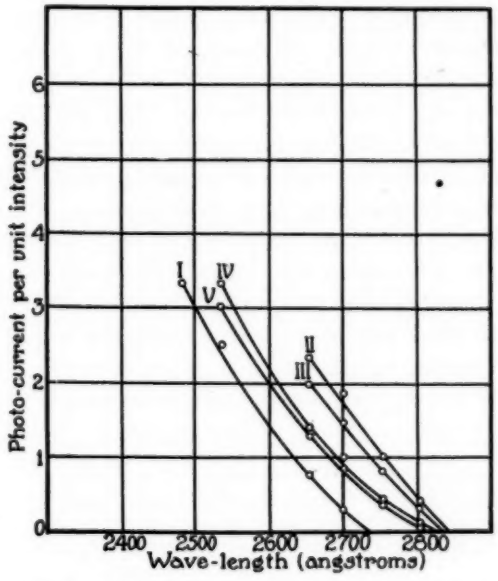

Fig. 4. Change of threshold with hydrogen in the still. I. Curve for flowing surface. II. 50 minutes after turning off still. III. 14 hours after turning off still. IV. 85 hours after turning off still. V. 110 hours after turning off still.

sensitivity had been reached, 50 minutes after turning off the still. The threshold shown is 2850A, the same as that reached when hydrogen is not present. The surface was then left standing, and curves III, IV, and V were taken after 14, 85, and 110 hours, respectively. If these are compared with the curves of Fig. 1, obtained similarly but without hydrogen present in the still, it is seen that the rate of fall of the threshold is now much less.

After curve V of Fig. 4 had been taken, the still was again started, the hydrogen being allowed to remain. After two hours of running, the normal threshold of 2735A was obtained. The time of rise after turning off the still was 44 minutes. The next day a repetition of the experiment gave 84

minutes, while three days later 124 minutes was required. This last result is shown in curve III, Fig. 3. In all cases the threshold reached the maximum of 2850A.

The hydrogen was then pumped from the still, the pumping being continued for several days and the still operated at the same time, in order to free the mercury from hydrogen as completely as possible. The time of rise was then found to be 20 minutes. Two weeks later it had fallen to 14 minutes. A second admission of hydrogen to the still increased the time again to 122 minutes, checking the former result.

From this behavior we may draw three conclusions: first, hydrogen does dissolve appreciably in the mercury and flow with it to the photo-cell; second, this dissolved hydrogen does not change the threshold of the clean running surface; third, the action of some other impurity is greatly impeded by the presence of the hydrogen. The explanation of this third result would seem to be that the hydrogen evaporates from the mercury surface and diffuses away from it, resulting in a lowering of the pressure of the other impurity in that vicinity.

The possibility of such an indirect effect of hydrogen, and perhaps of some other gases, should be considered in connection with many other photo-electric experiments. For example, Dümpelmann and Hein[4] have found that the photo-electric sensitivity of a metal plate is increased when either hydrogen or oxygen is generated electrolytically on the other side of the plate. It is probable that this is due, not to any direct effect of the gas upon the photo-electric properties of the metal, but rather to the driving away, by the gas diffusing through the plate, of some other impurity that has been holding down the sensitivity.

In conclusion, I wish to express my warmest thanks to Professor R. A. Millikan for his direction of the work here reported.

NORMAN BRIDGE LABORATORY OF PHYSICS.
CALIFORNIA INSTITUTE OF TECHNOLOGY.
September 30, 1926.

[4] R. Dümpelmann and W. Hein, Zeits. f. Physik, 22, 368 (1924).

ON ATOMIC PROPERTIES WHICH MAKE AN ELEMENT A METAL

By K. F. Herzfeld

Abstract

A criterion for determining when an element will show metallic conductivity.—From the dielectric constant of a gas or from its refractive index, extrapolated to long wave-lengths, the molar refractivity R can be calculated. In the solid or liquid state we have $(n^2-1)/(n^2+2)=Rd/M$. The left side cannot be larger than 1. If the right side becomes larger than 1, the dispersion electron is set free and the body then has metallic conductivity. The necessary and sufficient condition for metallic conductivity is therefore $R>M/d$. The prediction is verified in the case of metals for which the refractive index is known or for which it can be calculated. It is shown that the condition is probably satisfied in the case of metals for which the refractive index cannot be calculated with certainty. The conductivity of sodium dissolved in liquid ammonia is discussed.

FOR a transparent body the refractivity, $(n^2-1)/(n^2+2)$, is proportional to the density. That (n^2-1) does not vary proportionally with d is explained as follows. The polarization of a medium under the influence of an external electric force increases not only directly with increase in the number of molecules in unit volume, but also because of the presence of other polarized molecules near the one in question. These give rise to a force helping the external field, the so-called Lorentz-Lorenz force.

If p is the electric moment of a molecule and N the number of molecules per cm³, the polarization of 1 cm³ will be

$$P=Np$$

The polarization of a molecule under the action of an electric force E is proportional to the force, thus $p=rE$ and we have for higher densities the equation

$$p=r(E+4\pi P/3) \tag{1}$$

where the second term in the parenthesis is the Lorentz-Lorenz force. Writing N_L for the number of molecules in the mole, M for the molar weight and R for the molar refractivity, we have

$$4\pi Nr=4\pi N_L rd/M=3Rd/M.$$

Since $4\pi P/E=n^2-1$, we get

$$n^2-1=3R\frac{d}{M}\left(1+\frac{n^2-1}{3}\right) \tag{2}$$

or

$$(n^2-1)/(n^2+2)=Rd/M \tag{3}$$

As an example of the constancy of R we may recall that R for carbon disulfide vapor is 0.2805, while for the liquid it is 0.2898. The slight deviation of 3 percent between these two figures has to be explained by a real change in the molecule, a "deformation."[1] Of course the particular factor $\frac{1}{3}$ in Eq. (1) is valid only in isotropic or cubic substances.

Now it is quite clear that the value of the left side of Eq. (3) cannot be larger than 1. What happens, then, if we start with a substance of large refractive index in the gaseous state and compress it, increasing the value of Rd/M until it reaches 1? We may answer this question by considering the equation of motion of the dispersion electrons in the molecule according to the classical theory. In a single molecule this equation would be

$$m\ddot{p}+4\pi^2 m\nu_0^2 p=e^2 fE$$

where ν_0 is the characteristic frequency in the free molecule and therefore a measure of the force holding the electron in the molecule; f is the number of dispersion electrons.

For higher densities the above equation must be replaced by

$$m\ddot{p}+4\pi^2 m\nu_0^2 p=e^2 f(E+4\pi P/3)=e^2 f(E+4\pi Np/3)$$

or

$$m\ddot{p}+4\pi^2 m\nu_0^2(1-Ne^2 f/3\pi m\nu_0^2)p=e^2 fE \tag{4}$$

Now we have

$$Ne^2 f/3\pi m\nu_0^2=Rd/M \tag{5}$$

R being taken for infinitely long waves of incident light. Therefore the characteristic frequency of the electrons in the molecule is diminished to the value

$$\nu_0(1-Rd/M)^{1/2}$$

If Rd/M is equal to 1 the resultant force on the electron vanishes; the electron is set free.*

We conclude that the necessary and sufficient condition for a substance to have metallic conduction in the liquid or solid state is the following; It must have such a high value of R (which can be found by measuring the index of refraction in the vapor state for infinitely long wave-lengths) that

$$R>M/d \tag{6}$$

if the density of the solid or liquid state is inserted. This applies only if the vapor is monatomic, the solid nearly cubic or the liquid also monatomic.

[1] K. Fajans and G. Joos, Zeits. f. Physik **23**, 1 (1924).

* If we have a thin gas with N molecules, each with one isotropically bound electron the the system has $3N$ equal natural frequencies. Increase of the density increases the coupling, and this splits up the coincidence. We calculate the three equal lowest frequencies for which alone Equation 1 holds (homogeneous polarization). This mode of vibration is the only one excited by light waves.

TABLE I

Values of R and of M/d for certain elements.

The refractive index n is for the vapor at 0°C and 1 atm. The data for Na were taken from Wood's[2] paper, for the rare gases from the compilation of Herzfeld and Wolf,[3] the rest from Cuthbertson's[4] measurements.

Element	n	R	M/d (cm³)	Element	n	R	M/d (cm³)
Na	1.0041	61	23.6	He	1.0000347	0.518	27.4
Zn	1.00096	14.6	9.2	A	1.000278	4.15	27.8
Cd	1.00134	20.0	13	Kr	1.000418	6.25	38.4
Hg	1.00092	13.74	14.61 (liq.) 14.22 (sol.)	X	1.000682	10.2	37.3
S_2	1.00100	16.42	31	P_2	1.00120	17.9	26.6 (metal) 34 (white)
Se_2	1.00153	22.84	33 (metal) 37 (glass)	As_2	1.00155	23.1	26.2
Te_2	1.00237	35.4	40.8				

How well this condition is satisfied is seen by referring to Table I in which are presented the calculated values of R and of M/d for a number of substances whose refractive indices in the gaseous state are known. Of these elements, four are metals with monatomic vapor, Na, Zn, Cd, and Hg. Of these only Na is cubic but we expect no large deviation on account of this fact. For Na, Zn and Cd the relation (6) is fulfilled. For solid Hg Rd/M is 0.965 and the metallic state, which demands that this quantity be greater than 1, can be accounted for by a real change in R, a "deformation" as in the case of CS_2. For liquid Hg the calculated value is 0.94 and the metallic state could be accounted for by a formation of molecules Hg_2, if the distance of the two atoms in the molecule were about $\frac{3}{4}$ of the apparent average distance.

For the rare gases in Table I R is less than M/d as we should expect since they are non-metallic. For the remaining elements listed in the table, which have diatomic molecules, the formula cannot be applied rigorously. If we assume that it can be applied the non-metallic nature would follow from the results. It is gratifying to note that Rd/M has the highest value for Te and As (0.87 and 0.88).

There are no other direct measurements for R except for the gases H_2, O_2, etc., for which it is well known that the value of Rd/M for the condensed state is less than 1. In other gases we could calculate R from the formula

$$R=\sum Ne^2f/3\pi mv_i^2 \tag{7}$$

if we knew the electron number f for each absorption line. This number determines the strength of the absorption line.

[2] R. W. Wood, Phil. Mag. **8**, 293 (1904). The density was calculated with the ratio of fringe shifts at 496 and 644°C, and the absolute value at 500°C given by Zisch, Zeits. f. Physik **8**, 137 (1922). This value was checked by theoretical calculation according to Eq. (5).

[3] K. F. Herzfeld and K. L. Wolf, Ann. d. Physik **76**, 71 (1925).

[4] C. Cuthbertson and E. P. Metcalf, Proc Roy. Soc. **A80**, 411 (1908); Phil. Trans. **207**, 135 (1906).

For Na it has been shown that the index of refraction of the vapor can be fairly well calculated by taking $f=1$ for both resonance lines (D lines) together and neglecting the others.[5] We shall now assume the same to be true for the other alkali metals and for copper, silver and gold. The results of the calculations are presented in Table II and are interesting in the following respect. It may be suggested that the non-metallic character of an element is determined by its large energy of ionization, or in other words by the force which holds the electron in place, or by ν_0^2. While this is true in general, the real determining factor is the ratio of this force to the density fd/M of the dispersion electrons in space. For example, the silver atom with a shell of 18 electrons[6] holds its dispersion electron much more strongly than do the atoms of the alkali metals. If it had, in the solid state, the large molar volume of potassium (44.7) it would *not* be a metal. It is a metal in spite of the low value of R only because of its low molar volume. On the other hand if the rare gas xenon, with $R=10.2$, had in the solid state the low molar volume of copper, 7.1, it would be a metal.

TABLE II

Values of R and of M/d for certain metals. R is calculated by means of Eq. (7).

	Li	Na	K	Rb	Cu	Ag	Au
Resonance line λ :	6708	5890	7664	7800	3247	3280	2427
R :	81.5	62.7	107	110	18.95	19.4	10.7
M/d :	13	23.6	44.7	55.8	7.1	10.2	10.2

For other metals the calculation cannot be made with any certainty. We give in Table III after the symbol of the element the wave-length of the resonance line used,[7] then the value of R calculated with only one electron contributing to the strength of the line and neglecting other lines, then the molar volume M/d, the minimum f necessary to make the element a metal if no other line contributes, and finally the total number of electrons in the last n_k group. It must be remarked that Kuhn[8] found for the line 2768 in Tl a value for f of only 0.24, while for the other strong line, 3775, (which for $f=1$ would alone give R a value of 25.7) he found a value for f of but 0.1. With these values for f the two lines together would result in a value for R of but 5.58. So long as we do not know more of the absolute intensities of the absorption lines we cannot give decisive data for the metals listed in Table III.

In this connection we may remark that the condensation of carbon atoms to diamond must result in a marked change in the electron orbits, for otherwise, with the small molar volume of diamond (3.4) and with $f=2$, the diamond would be a metal even if the resonance line had a wave-length as short as 970A.

[5] Chr. Fuchtbauer and W. Hofmann, Ann. d. Physik **43**, 96 (1914). R. Ladenburg and R. Minkowski, Zeits. f. Physik **6**, 153 (1921).

[6] H. G. Grimm, Zeits. f. Phys. Chem. **98**, 359 (1921).

[7] Taken from H. N. Russell, Astrophys. J. **61**, 223 (1925).

[8] W. Kuhn, die Naturwiss. **13**, 725 (1925).

TABLE III

Values of R and of M/d for certain metals.

R is calculated from Eq. (7) assuming $f=1$ for the single resonance line given in the second column.

Element	λ	$R(f=1)$	M/d	f(min)	Electron number in last group
Be	2348	10.0	5.2	0.52	2
Mg	2852	14.7	14.1	0.96	2
Ca	4226	32.0	25.9	0.81	2
Sr	4607	38.4	34.5	0.90	2
Ba	5535	55.4	36	0.65	2
B	2498	11.3	4.5	0.4	1
Al	3961	29.3	10	0.34	1
Ga	4033	29.3	11.8	0.40	1
In	3256	19.1	16.1	0.84	1
Tl	2768	13.8	17.2	1.25	1
Pb	2833	14.5	18.25	1.26	2
Ti	3998	29.0	10.7	0.37	4
V	3841	26.6	9.28	0.35	5
Cr	4254	32.7	7.76	0.24	6
Mo	3902	27.6	10.65	0.39	6
Mn	4030	30.0	7.4	0.25	7
Fe	3720	25.9	7.1	0.27	8
Co	3465	21.6	6.8	0.31	9
Ni	2320	9.7	6.7	0.69	10
As	2349	10	13.1	1.31	3
Sb	2311	9.75	18.5	1.9	3
Bi	3067	17.0	21.5	1.27	3

It is well known that according to Kraus[9] sodium dissolved in liquid ammonia is a conductor. If the molar conductivity is plotted against concentration it shows first for increasing concentration a decrease, as usual in electrolytes. But above 1 mole in 20 liters there is a slight increase and above 1 mole in 900 cm³ there is a strong increase in conductivity with concentration. From considerations similar to those already mentioned we should expect that in ammonia the valence electrons are set free by mutual action of neighboring sodium atoms at concentrations above 1 mole in 500 cm³, while for lower concentrations the conductivity would be due only to the action of ammonia on the sodium.

JOHNS HOPKINS UNIVERSITY
PHYSICAL LABORATORY
February 26, 1927.

[9] C. A. Kraus, Jour. Am. Chem. Soc. **43**, 749 (1921).

THE ABSORPTION OF RADIO WAVES IN THE UPPER ATMOSPHERE*

By E. O. Hulburt

Abstract

Recent measurements have shown that radio waves below 150 meters fall off in intensity faster than required by an inverse square law for distances up to 1000 miles. This points to absorption of the wave by the medium, in this case the upper atmosphere. The absorption of the waves variously polarized is calculated on the assumption that it results from collisions between the electrons and molecules of the atmosphere. With reasonable average values of the electronic and molecular densities the amplitude A of the wave λ cms at a distance x cms is $A=\alpha x^{-1}\, exp\, (-11.8\times10^{-16}\lambda^2 x)$, theoretically valid for waves from 16 to 160 meters to distances of 1000 miles. This agrees well enough with the scant range and intensity data, and it is pointed out that an extension of these data may lead to more exact knowledge of the overhead electronic and molecular pressures. From the absorption curves interesting possibilities appear of polarization of waves in the broadcast band 200–600 meters.

IN RECENT papers[1,2] a quantitative theory of the manner in which radio waves pass over the earth has been developed. The waves are shown to reach distant points on the surface of the earth by passage through the outlying regions of the earth's atmosphere being refracted downward by the electrons of those regions. From the simple fact that radio waves, particularly of wave-length below 90 meters, are transmitted successfully with relatively small amounts of power to distances as great as half-way around the earth, it was assumed that the attenuation of the waves in the upper atmospheric strata was slight. As a matter of fact absorption of energy from the wave by the atmosphere was put aside entirely, but the calculations were made in such a way as to be undisturbed by a small absorption which of course exists. In the present paper the influence of absorption is considered with the result that certain facts about the ranges of the waves of the radio spectrum begin to be more clearly understood.

The optical properties of the upper reaches of the atmosphere are assumed to depend upon the molecules, ions and electrons which exist there. The magnetic field of the earth has an important influence which is recognized in the formulas. The electrons contribute largely to the dispersion of the electromagnetic waves, the molecules and ions only a secondary part in so far as they interfere with the electrons. All, however, contribute to the absorption, for we shall assume that the most important cause of the absorption of energy from the wave arises from collisions between the electrons and molecules. The effect of collision is to transfer a portion of the energy which the electron has received from the waves to the molecule and produce the

* Published by permission of the Navy Department.

[1] Taylor and Hulburt, Phys. Rev. **27**, 189 (1926).

[2] Hulburt, Journal of the Frank. Inst. **201**, 597 (1926).

disorderly motion called heat. The ions may justifiably be treated as molecules, for the effect of their charges on the dispersion and absorption is negligible (see reference 2, page 610). With these assumptions the general formulas for the dispersion and absorption are all available in treatises on magneto-optics, for example Lorentz[3], and therefore for the special formulas developed here we need only record a few of the more essential steps. If an electron of mass m experiences f collisions per second with the molecules, it has been shown[4] that this may be expressed as a frictional force gv on the electron, where v is the velocity of the electron and g is given by

$$g=2mf. \tag{1}$$

In this formula the collisions are regarded as inelastic; this is a true absorption of energy. Other types of collisions may occur, such as elastic ones which cause scattering of the energy, etc. A more extended treatment may therefore be expected to modify (1). The change will probably not be great and for the present, at any rate, we shall be content to use (1) as it stands.

In writing down the equations of motion of the electron we assume no restoring force due to the medium and no effect of the electrons of each other. Let E_x and ξ be the X components of the electric force and the displacement of the electron, respectively, and η, ζ, E_y and E_z the Y and Z components of the quantities. N is the number of electrons per unit volume, e and m are the electronic charge and mass. The earth's magnetic field H is in the direction of the axis of Z. In c.g.s. electromagnetic units the equations of motion of the electron are

$$\left.\begin{aligned} m\ddot{\xi} &= eE_x - g\dot{\xi} + He\dot{\eta}, \\ m\ddot{\eta} &= eE_y - g\dot{\eta} - He\dot{\xi}, \\ m\ddot{\zeta} &= eE_z - g\dot{\zeta} \end{aligned}\right\} \tag{2}$$

The exact solutions of (2) are extremely cumbersome. The solutions become much simpler, however, if (following Lorentz) the approximation is adopted that the absorption is small in the space of a wave-length; fortunately this approximation is entirely acceptable in the case of the radio waves.

For incident plane waves advancing in the direction of H the approximate solution of (2) yields two circularly polarized components of refractive indices μ and absorption coefficients κ given by

$$\mu^2 = 1 - \frac{C\lambda^2(1-\lambda/\lambda_0)}{(1-\lambda/\lambda_0)^2+G^2\lambda^2}, \tag{3}$$

$$\kappa = \pi CG/\left[(1/\lambda - 1/\lambda_0)^2+G^2\right], \tag{4}$$

[3] H. A. Lorentz, "The Theory of Electrons," Chap. IV (1916).

[4] Lorentz, Loc. cit., p. 309 or more recently, Houston, Phil. Mag. 2, 512 (1926).

and

$$\mu^2=1-\frac{C\lambda^2(1+\lambda/\lambda_0)}{(1+\lambda/\lambda_0)^2+G^2\lambda^2}, \tag{5}$$

$$\kappa=\pi CG/[(1/\lambda+1/\lambda_0)^2+G^2], \tag{6}$$

where

$$C=Ne^2/\pi m, \quad \lambda_0=2\pi cm/He, \quad G=g/2\pi cm=f/\pi c \ \ [\text{From (1)}], \tag{7}$$

c being the velocity of light in vacuum. With the value 0.5 gauss for H, λ_0 from (7) comes out to be 214 meters. The absorption coefficient κ is defined by the relation

$$A=A_0\epsilon^{-\kappa x} \tag{8}$$

where A_0 is the initial amplitude of the wave and A the amplitude after traversing x cms of the medium.

For incident plane waves advancing normally to the magnetic field the solution of the equations of motion yields two plane polarized components, respectively parallel and perpendicular to H, of refractive indices μ and absorption coefficients κ given by

$$\mu^2=1-\frac{C\lambda^2}{1+G^2\lambda^2}, \tag{9}$$

$$\kappa=\pi CG/(1/\lambda^2+G^2), \tag{10}$$

and

$$\mu^2=\frac{(A^2+B^2)^{1/2}+A}{2Q}, \tag{11}$$

$$\kappa^2=\frac{2\pi^2}{\lambda^2}\,\frac{(A^2+B^2)^{1/2}-A}{Q}, \tag{12}$$

where

$$A=pq+rs, \quad B=ps-rq, \quad Q=q^2+s^2; \quad p=(1+\alpha)^2-\gamma^2-\beta^2,$$
$$r=2\beta(1+\alpha), \quad q=\alpha(1+\alpha)-\gamma^2-\beta^2, \quad s=\beta(1+2\alpha);$$
$$\alpha=-1/C\lambda^2, \quad \beta=CG/\lambda, \quad \gamma=1/C\lambda\lambda_0.$$

Expression (10) is an approximation based on small absorption, just as was the case in (3) and (4); it refers to the component with electric vector along H, and therefore to propagation in the absence of the magnetic field. Expression (12), however, which refers to the electric vector normal to H, is exact; the approximation of small absorption did not lead to much simplification. For no absorption, $g=G=\kappa=0$, and the four formulas for μ, (3), (5), (9) and (11), reduce respectively to the formulas (2), (3), (5) and (6) of the earlier paper.[1]

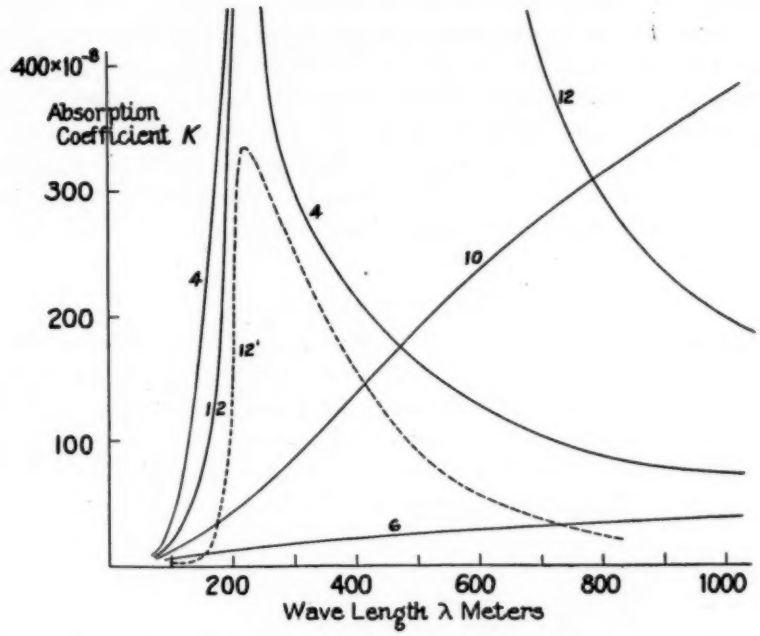

Fig. 1. Absorption coefficients of the upper atmosphere as a function of the wave-length for rays in and perpendicular to the earth's magnetic field, from equations (4), (6), (10) and (12). Curve 12′ is curve 12 with ordinates reduced ten times.

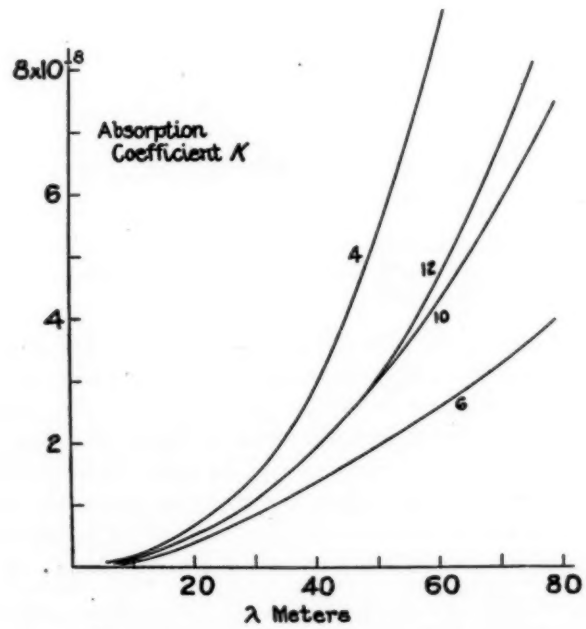

Fig. 2. The short wave portion of Figure 1 on a larger scale.

To bring out the general character of the absorption, κ from formulas (4), (6), (10) and (12) is plotted in curves 4, 6, 10, and 12, Fig. 1, respectively with $\lambda_0 = 214$ meters, $C = 2.5 \times 10^{-11}$ or $N = 280$ electrons per cc, and with $G = 1.5 \times 10^{-5}$. Curve 12 rises to such high values as to be off the page, so that it has been drawn again in curve 12′, Fig 1, on the same abscissas, but with ordinates ten times reduced Since we shall be interested in the curves in the region of shorter waves below 100 meters, the respective formulas for κ have been plotted on a larger scale in the curves 4, 6, 10, and 12 of Fig. 2.

Experimental Data

A program of measurements of the electric field A of the received wave at various distances from the transmitter for the shorter waves, below 200 meters, has recently been entered upon by Heising, Schelleng and Southworth.[5] We choose a portion of their data for wave-lengths 44 and 66 meters under full daylight conditions; these are plotted respectively in curves 1 and 2, Fig. 3, in which the ordinates are the field strengths A in arbitrary

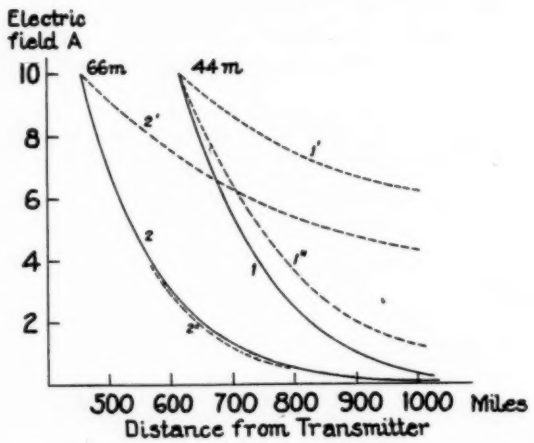

Fig. 3. The electric field as a function of the distance from the transmitter for a 44 and a 66 meter wave; curves 1 and 2 observed, curves 1′ and 2′ calculated by the inverse distance law, curves 1″ and 2″ calculated from (15).

units and the abscissas are the distances from the transmitter in miles. The curves do not claim great accuracy, their smoothness in the drawing really gives a wrong impression of the precision. They represent averages of field strengths which fluctuated over wide limits from day to day. Qualitative observations of the strengths of signals with waves below 100 meters have been recorded by Prescott,[6] these are, however, unsuited to quantitative calculations. We shall have use for Taylor's[7] ranges of transmission. These ranges in miles, under full daylight, averaged throughout a year for uniform

[5] Heising, Schelleng and Southworth, Proc. Inst. Rad. Eng. **14**, 613 (1926).
[6] Prescott, "QST" **10**, 9 (1926).
[7] Taylor, Proc. Inst. Rad. Eng. **13**, 677 (1925).

transmitting conditions, i.e. five kilowatts in a normal transmitting antenna, are plotted in curve 1, Fig. 4 as ordinates against the wave-lengths as abscis-

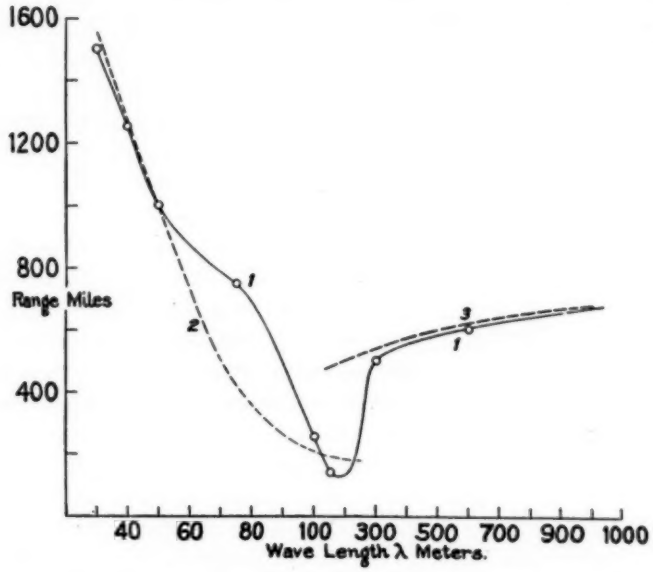

Fig. 4. The average daylight ranges, for uniform transmitting conditions, as a function of the wave-length; curve 1 observed, curves 2 and 3 calculated from (15) and (14) respectively.

sas. For the sake of clearness the scale of the abscissas for waves below 100 meters is ten times that for waves above 100 meters.

Application of the Formulas

Before entering upon a discussion of the experimental data in the light of the theoretical formulas, it is well to fix ideas by referring to Fig. 5, which shows the ray path *ace* of a 66 meter wave, and *afe* of a 44 meter wave, from

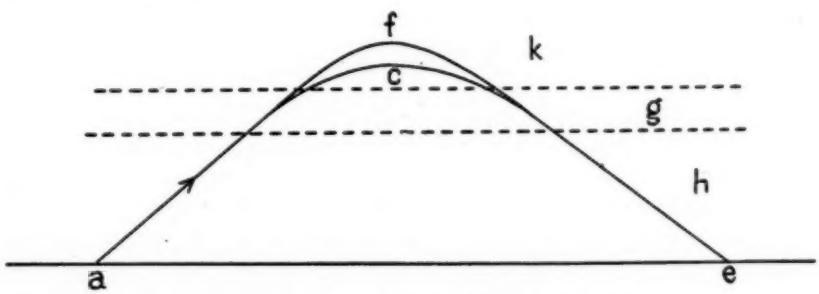

Fig. 5. Refraction of rays in the electronic regions g and κ.

the transmitter a to the receiver e. In the region h of the atmosphere there are no electrons and the rays are straight. In the region g, marked off from h by a dotted line in Fig. 5 there are a considerable number of electrons and air molecules; it is here that the absorption may be supposed to

occur. Above this there is a region k of greater electronic density, but of lower molecular density, so that the absorption is again slight. The electronic density increases with the height reaching a value of the order of 10^5 at about 100 miles above the earth (an average for daylight over a year[1]). In the regions g and k the rays bend over and return to the earth, and as seen from the refraction formulas (3), (5), (9) and (11) the 66 meter path is below the 44 meter ray. There is evidence[8] that the electron density sets in rapidly above h so that the curved portions of the ray paths are relatively short compared to the whole length of the path, and therefore the paths of a 44 and a 66 meter wave, for example, will not differ greatly.

We may now turn to the data of curves 1 and 2, Fig. 3, which have been chosen for numerical discussion for particular reasons. These curves give the electric fields of the 44 and 66 meter waves at distances from 600 to 1000 miles from the transmitter. At these distances the direct ground wave was absent so that the field strengths were due to rays refracted downwards from the upper atmosphere. Furthermore, multiple reflections and focussing of the rays by the electronic regions are probably of small influence here, so that for a given wave-length and state of polarization a single ray from the transmitter to a receiver may be assumed. The transmitter is considered to deliver its rays impartially in all directions to perhaps 30° above the horizontal. We shall further assume that the length of the ray path may be roughly calculated as if the ray travelled in a straight line to a height of 100 miles and there experienced sharp reflection. Thus, the ray path distance x is related to d, the great circle distance to the transmitter, by the equation, $x=(d^2+4h^2)^{1/2}$, h being 100 miles, and for $d>400$ miles, $x=d$, approximately. If the electric field of the wave diminished inversely with the distance (i.e. the energy inversely with the square of the distance) the field strength would be shown in curves 1′ and 2′ of Fig. 3. In short, the observed field strengths fall off much more rapidly with the distance than the inverse first power; this too for the case, purposely selected, in which one might expect the inverse first power law to hold full sway. Evidently an additional cause of energy degradation is at work, and we take this to be the absorption of energy from the wave by the atmosphere.

We then write

$$A=A_0(x_0/x)\epsilon^{-\kappa(x-x_0)}, \tag{13}$$

where A and A_0 are the field strengths at ray path distances x and x_0, respectively, and κ is the absorption coefficient defined in (8).

For the moment we must leave the ray picture of Fig. 5, to return to it later, and assume that the optical properties of the atmosphere are constant along the entire path of the ray. The absorption coefficient κ may then be calculated for $\lambda 66$ meters by substituting in (13) the coordinates of the ends of curve 2, Fig. 3, and comes out to be 5×10^{-8}. With this value of κ the curve 2″ was calculated corresponding to the observed curve 2; it is seen that the two curves are in close agreement. We might now determine κ for $\lambda 44$

[8] Breit and Tuve, Phys. Rev. **28**, 554 (1926).

meters from curve 1, Fig. 3, in a similar manner, and then by substituting the respective values of κ for $\lambda 44$ and $\lambda 66$ meters in, say, formula (10) obtain two equations in the two unknowns C and G, and thereby determine C and G. Unfortunately such a procedure yields meaningless values for C and G, merely because the data of curves 1 and 3, Fig. 3, are not sufficiently accurate. It seems therefore best to proceed by making a frank assumption, namely, that throughout the course of the ray the average number of molecules per cc is 5×10^{14}; this pressure corresponds to a height above the earth of about 50 miles.[9] With a value $-50°$C for the temperature the number of collisions f which an electron makes per second with the molecules is calculated from classical kinetic theory to be 1.4×10^{6}. From (1) and (7) this gives $G=1.5\times10^{-5}$. Referring only to the state of polarization represented by (10) we introduce the value of G into (10) together with $\kappa=5\times10^{-8}$ for $\lambda 66$ meters, and find $C=2.5\times10^{-11}$ and 280 for the electronic density N. With the constants thus determined κ is calculated from (10) to be 2.29×10^{-8} for $\lambda 44$ meters, and the intensity degredation curve for this wave-length corresponding to the observed curve 1, Fig. 3, is calculated. This is given in curve 1″, Fig. 3, and is seen to agree with curve 1 within the error of observation.

It is of interest to see what can be done with the range curve 1 of Fig. 4, which gives the ranges reached by the various waves. We take this to mean the distance at which the wave amplitude is a constant small value, i.e. the value just detectable. (It will be appreciated that this is exactly the case of the intensity distribution curves of spectrum lines or bands derived from neutral wedge spectra.) Thus A in (13) is a constant, and (13) can therefore be used to calculate the ranges x or d, (x being the ray path distance and d the great circle distance) for values of λ by using the κ corresponding to each λ determined from (10) with the constants $C=2.5\times10^{-11}$ and $G=1.5\times10^{-5}$ given in the preceding paragraph. The quantity x_0 being entirely arbitrary is taken to be small with respect to x so that it disappears from the exponent in (13). The calculated range curve, made to pass through one observed point, i.e. 1000 miles for $\lambda 50$ meters, is given in the dotted curve 2 of Fig. 4 and agrees with the observed curve within the error of experiment for the waves from 16 to 150 meters. For waves longer than 200 meters the calculated ranges are below the observed values, as indeed is to be expected, since for these wave-lengths the ground wave is predominant at the shorter distances and the overhead ray is relatively feeble.

At first sight the fair agreement which has been reached between theory and experiment might appear meaningless. So many simplifying assumptions have been made that the theoretical picture might seem to have but little resemblance to reality. The considerations which follow, however, indicate the agreement to be genuine and to offer strong support of the theoretical ideas. The foregoing calculations are valid, within limits, for the general case of random polarization, in spite of the fact that they have been based on the absorption formula (10) which refers to a ray polarized in a particular

[9] Humphreys, "Physics of the Air," 1920.

way. For, an exactly similar calculation with each of the other types of polarization represented by (4), (6), and (12) yields agreement with the experimental curves of Fig. 3 and 4 similar to that obtained with (10). This comes about because the values of κ from one of the curves of Fig. 2 are roughly proportional to those from any of the other curves. We have assumed that the rays pass through a homogeneous medium composed of, for example, 5×10^{14} molecules and 280 electrons in each cc, these numbers giving the desired values for the absorption. However, because of the approximately linear relation between κ, N and the molecular density we may keep the absorption values undisturbed and at the same time suppose that the absorption exists only in a certain fractional part of the ray path (the electrons having a density greater than 280, of course). Thus we return to the more exact conception of the ray paths sketched in Fig. 5, in which the absorption occurs only in the region g. The numbers 5×10^{14} and 280 are therefore to be regarded as properly chosen equivalent average values over the ray path.

The values of the molecular and of the electronic density are of course in no wise fixed by the foregoing calculations. The one has been a proper guess and the other has been calculated from it; when regarded as average values over the ray path the numbers are perhaps reasonable. With the experimental radio data at present this is about all that can be done. As these data improve and become more numerous we may hope that they may be fitted into a general scheme which in the end will depict the electronic and molecular pressures at all heights above the earth to which we may direct a radio ray so that it will return. We may take this occasion to mention that throughout this and the earlier papers[1,2] we have been at pains as far as possible to draw conclusions as to the electrons, etc., of the upper atmosphere from the radio wave phenomena only. With the idea, wise or unwise, that these inferences may be entirely independent of, and therefore worthy of comparison with, similar inferences from other fields of experiment[10,11]. Meanwhile others[12,13] have been attacking the converse problem of calculating the ionization by means of the absorption of radiation, or in other ways, and from this to derive the facts of radio. However, we prefer to regard the radio waves as a means, and a fruitful one, of plumbing the outer depths just as the earthquake waves of seismology serve to search the earth beneath.

From the present viewpoint two programs, rather prosaic perhaps, of experimental measurements suggest themselves, namely, measurements of average field intensities of waves below 200 meters and observations of the polarizations of waves, say, 100 to 1000 meters, throughout distances to 2000 miles or more from the transmitter. The first is an extension of the curves of Fig. 3 and the work of Austin,[14] the second is touched upon,

[10] Chapman, Roy. Meteor. Soc., Quarterly Journal **52**, 225 (1926).

[11] Bendorf, Phys. Zeitschrift **27**, 686 (1926).

[12] Rice and Baker, Journ. Amer. Inst. Elect. Eng. **45**, 535 (1926).

[13] Lassen, Zeits. f. Hochfrequentztechnik, **28**, 109 and 139 (1926); Elias, ibid., **27**, 66 (1926).

[14] Austin, Bull. Bur. Stand. **7**, 317 (1911).

although slightly, in the experiments of Picard,[15] of Smith-Rose and Barfield,[16] and of Appleton.[17] One must however, refrain from being too sanguine of the success of such programs. An experimental analysis of the received wave to discover its state of polarization is not simple. The ground causes complicating effects and the state undoubtedly varies more or less rapidly with the time. Particularly in the broadcast range of wave-lengths from 200 to 600 meters a glance at the absorption curves of Fig. 1 and the refraction curves (readily plotted from (3), (5), (9), and (11).) indicates a rather bewildering array of possible states of polarization. Apparently one might simplify things by dealing with east-west or north-south propagation, particularly at the equator where the earth's magnetic field is horizontal, or at the magnetic poles where it is vertical.

A discussion of the amplitudes of radio waves as a function of the distance from the transmitter is hardly complete without reference to the experimental measurements of Austin[14] on waves longer than 300 meters. These, for daylight conditions, are expressed in condensed form by the Austin-Cohen formula, which may be written

$$A = (aA_0/d)\epsilon^{-bd/\lambda^s}, \tag{14}$$

where a, b and s are constants and d is the great circle distance to the transmitter. If the curves of Fig. 3 are calculated from (14) values much too low are found, as indeed is to be expected since (14) is not valid for the shorter waves. Using (14), with Austin's values for b and s, to calculate the range curve of Fig. 4 we obtain the dotted curve 3, which agrees very well with the observations at the longer wave-lengths. This merely means that Taylor's independent measurements were consistent with those of Austin. Formulas (13) and (14), although somewhat similar, should not be confused; they supplement each other. (13) gives the theoretical received amplitude due to a single overhead ray, for waves below 150 meters, whereas (14) gives the actual received amplitude, which in the general case may be due to several overhead rays and a ground ray, for waves longer than 300 meters. The complete theoretical amplitude degradation formula embracing all wave-lengths will perhaps be similar in form to these. Even now for practical purposes formula (13) with the value of κ from (10) may be used to calculate the relative amplitudes of the shorter waves at various distances from the transmitter under full daylight conditions. We obtain to a sufficiently close approximation,

$$A = (\alpha/x)\epsilon^{-\pi CG\lambda^2 x} = (\alpha/x)\epsilon^{-11.8\times 10^{-16}\lambda^2 x}, \tag{15}$$

where α is a constant and λ and x are in cms, x being the ray path distance. (15) is valid for wave-lengths from 16 to 150 meters to distances of 1000 miles from the transmitter, and therefore covers as great a range of frequencies and distances as the Austin-Cohen formula. Because of the direct ground wave

[15] Picard, Proc. Inst. Rad. Eng. **14**, 205 (1926).
[16] Smith-Rose and Barfield, Proc. Roy. Soc. **110A**, 580 (1926).
[17] Appleton, Proc. Roy. Soc. **109A**, 621 (1926).

the formula does not hold too near the transmitter, for 75 meters waves within, say, 100 miles, and for longer waves within longer distances. The ground wave, however, can be calculated from the Sommerfeld formula.[18] Expression (15) of course is not true at great distances. For instance, in the case of a 30 meter wave it gives at 5000 miles from the transmitter 10^{-7}, and at 3000 miles 10^{-4}, of the energy at 1000 miles, and qualitative experience indicates that the signal strengths are usually greater than these numbers. At great distances the showering down of energy from the upper atmosphere, or, in other words, the contribution of many possible ray paths, is sufficient to overshadow an inverse square law of energy attenuation further weakened by exponential absorption.

NAVAL RESEARCH LABORATORY,
WASHINGTON, D. C.,
January 7, 1927.

[18] Sommerfeld, Ann. d. Phys. **28**, 665 (1909).

ELECTRICAL MEASUREMENTS AT RADIO FREQUENCIES

By S. L. Brown and M. Y. Colby

Abstract

Methods of measuring resistance, inductance, capacity, and impedance at radio frequencies.—Resistance, inductance, capacity, and impedance are measured at radio frequencies with the aid of a vacuum tube voltmeter. The experiments described and the data presented illustrate methods of measurement at radio frequencies that are comparable to the corresponding measurements at low frequencies with regard to both simplicity and accuracy. The results indicate that the resistance of a circuit may be measured with an accuracy of one percent at a frequency of several million cycles per second when the value of the resistance is of the order of 0.01 ohm. Much lower values can be measured with a reasonable degree of accuracy. The calculated value of the high frequency resistance of No. 22 copper wire differs from the measured value by less than one percent. The inductance of a portion of a circuit may be measured by a voltmeter-ammeter method with an accuracy of one percent, even though the value of the inductance be only a small fraction of a micro-henry. The calculated values of the inductance of either a circular coil of one turn or two parallel wires forming a return circuit agree with the measured values. Capacities of the same order of magnitude as the smallest readable variation of the variable standard condenser which is used to tune the circuit may be very quickly and easily determined. The measured and the calculated values of the capacity of two parallel wires are in very close agreement. Certain rolled plate types of telephone condensers have sufficient internal inductance to cause them to resonate at low radio frequencies.

The methods of making many radio frequency measurements have been improved: (a) By using such a low resistance circuit that the coupling to the source of power could be made very loose. The coefficient of coupling was frequently as low as 1×10^{-6}. (b) By using a negligible amount of power from the oscillator, with the result that the e.m.f. induced in the tuned circuit remained constant. The power drawn seldom exceeded 2×10^{-5} watts. (c) By employing a sensitive and accurate voltmeter that is independent of frequency. Voltage changes of 0.2 millivolts could be detected by this instrument.

THE problem of simplifying many measurements at radio frequencies was undertaken by the authors nearly two years ago, after the development of a sensitive vacuum tube voltmeter[1] which is reliable for all frequencies, including the higher radio frequencies. The accurate measurement of such fundamental quantities as resistance, inductance, capacity, and impedance at radio frequencies may be facilitated by the use of this instrument. When the quantities to be measured are small, a sensitive vacuum tube voltmeter may be advantageously used in reducing the difficulties encountered in making these measurements, and an accuracy comparable to that obtained in low frequency measurements can be obtained. The experiments described in this paper were designed to illustrate the advantages that are gained by adapting this voltmeter to radio frequency measurements.

[1] M. Y. Colby, Jour. Sci. Instruments III, 342 (1926).

Measurement of a Small Resistance

The resistance of an oscillating circuit having very low resistance may be readily determined by a slight modification of the resistance variation method. A diagram of the circuit, the resistance of which is measured, is shown in Fig. 1. The inductance L was made of one turn of No. 0000 copper

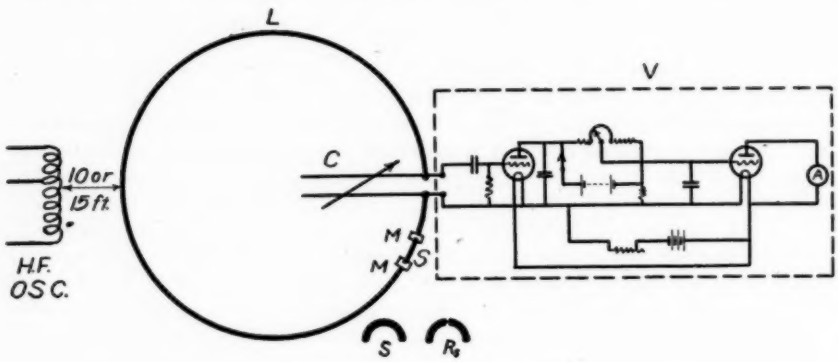

Fig. 1. Diagram of circuit for measuring high frequency resistance.

wire of one foot radius and the condenser C was a low-loss variable air condenser of the Bureau of Standards type. This circuit was very loosely coupled to an oscillator and was then tuned to resonance with it. The e.m.f. E_0 across the terminals of the condenser was measured by the vacuum tube voltmeter V. The short-circuit S was next removed and the standard resistance R_s substituted. The new value of e.m.f. E_s across the condenser was observed, and the resistance R_x of the circuit was calculated from the relation,

$$R_x = \frac{R_s}{E_0/E_x - 1}.$$

The values of R_x were always checked by using two standard resistances of different values. Values of the resistance of the circuit shown in Fig. 1, determined by this method, are given in Table I for several different frequencies.

Table I

High frequency resistance of a low resistance circuit

λ	C	R_s	E_0	E_x	R_x
119 m.	3885 $\mu\mu$f.	.0626 ohms	.372 v.	.151 v.	.0428 ohms
119	3885	.0253	.360	.226	.0427
102	2866	.0626	.385	.166	.0476
102	2866	.0253	.383	.250	.0476
82	1827	.0626	.354	.171	.0585
82	1827	.0253	.368	.258	.0592
58	949	.0626	.368	.214	.0870
58	949	.0253	.370	.286	.0864
43	513	.0626	.350	.240	.1365
43	513	.0253	.394	.333	.1380

The short-circuit S was made of about two inches of No. 0000 copper wire, bent so as to fit into the mercury cups MM. The standard resistance R_s was an exact duplicate of the short circuit S, except that about one-eighth of an inch of the large copper wire was cut out and replaced by an equal length of manganin wire of small enough cross section that the skin effect was neglibible. The use of this type of short-circuit and standard resistance insures a constant coefficient of coupling by making it unnecessary to change the shape, size, position, or configuration of the circuit when inserting or removing the standard resistance.

When the resistance of a circuit is very low, this plan of measurement, in terms of the e.m.f. across the reactance of the tuned circuit, is obviously superior to the usual plan, which involves the determination of the resonant current by means of an ammeter included in the tuned circuit. The chief advantage of this modification of the resistance variation method of measuring resistances over that usually practiced is that the resistance of the measuring instrument is not included in the resistance to be measured. In the case described here, the resistance of the circuit is so small that it might easily be concealed in the error of measurment if it is increased by the amount of the ammeter resistance.

To illustrate how a small resistance may be measured at radio frequencies, the circuit of Fig. 1 was employed. A length of approximately 1.5 inches of No. 22 copper wire was used. Short pieces of No. 0000 copper wire were soldered to its ends for making contact in the mercury cups MM. The circuit LC was very loosely coupled to an oscillator by placing the axis of the oscillator coil nearly at right angles to that of L and at a distance of 10 or 15 feet from L. The circuit was then tuned to resonance with the oscillator, and readings of the voltmeter V were taken with S, R_s, and the unknown resistance R_x, respectively, in the circuit. Calling the corresponding electromotive forces E_0, E_s and E_x,

$$R_x = R_s \frac{E_0/E_x - 1}{E_0/E_s - 1}.$$

The results obtained by this method are listed in Table II.

TABLE II

Resistance of a short piece of No. 22 copper wire at a frequency of 3,000,000 cycles per second.

Trial	E_0	E_x	E_s	R_s	R_x
1	.339	.281	.221	.0253	.0098
2	.341	.282	.224	.0253	.0102
3	.369	.305	.240	.0253	.0099

D. C. resistance of R_x measured by bridge	.00231 ohms
Diameter measured with micrometer calipers	.062 cm
Wave length measured with wave meter	100 meters
R_x calculated by Bureau of Standards formula[1]	.0100 ohms
R_x observed, (average)	.00997 ohms.

[1] Bureau of Standards Circular No. 74.

Using a circuit similar to that shown in Fig. 1, the high frequency resistance of a fixed condenser of large capacity was determined. A low resistance coil having the proper inductance to cause the circuit to resonate at the desired frequency was used for L. The resistance of the circuit consisting of the coil L and the variable air condenser C was measured by the method previously described. The high capacity fixed condenser was then inserted in series with L and C, and the resistance of the circuit again measured; the resistance of the fixed condenser was, then, the difference between the two values thus obtained. This method is accurate when the capacity of the fixed condenser is large enough in comparison with that of the variable condenser C so that it is unnecessary to change the setting of C materially in order to retune the circuit after introducing the fixed condenser. Typical results of this measurement are shown in Table III.

TABLE III

High frequency resistance of fixed condensers.

Type of Condenser	Wave Length	Resistance of circuit before inserting condenser	Resistance of circuit after inserting condenser	Resistance of condenser
1 microfarad high voltage paper condenser	645 m.	0.213 ohms	0.295 ohms	0.082 ohms
	405	0.358	0.465	0.107
.36 microfarad paper telephone condenser (Figure 6)	645	0.213	3.36	3.15
	500	0.28	4.08	3.80
	405	0.36	4.48	4.12

MEASUREMENT OF A SMALL INDUCTANCE

The value of a small inductance of negligible resistance may be determined by sending a measured current of known frequency through it and measuring the electromotive force across its terminals with the vacuum tube voltmeter. Thus the measurement of a small inductance at radio frequencies is reduced to the simple voltmeter-ammeter method.

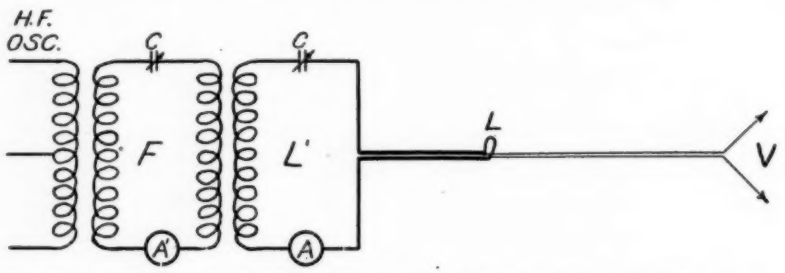

Fig. 2. Diagram of circuit for measuring the inductance of a small loop.

The inductance L of Fig. 2, consisting of a small circular coil of one turn, made of No. 14 copper wire, was connected in series with a coupling

coil L', a tuning condenser C, and an ammeter A. This circuit was coupled to the high frequency oscillator through the intermediate tuned circuit F, which was used to filter out any harmonics that might be present in the oscillator circuit. The result of a typical measurement is given in Table IV.

TABLE IV

Measurement of a small inductance

Diameter of coil	3.70 cm.
Diameter of wire	.163 cm.
Ammeter reading	103 m. a.
Voltmeter reading	204 m. v.
Wave-length (by wavemeter)	710 meters
$L(=E/I\omega)$	.0749 μh.
L calculated from dimensions[3]	.0753 μh.

The diagram of Fig. 3 shows two No. 10 copper wires WW 1645 cm long, stretched parallel to one another and spaced 10 cm apart. These wires were connected in series with an inductance coil L, a tuning condenser C, and an ammeter A. This circuit was coupled with a high frequency oscillator through the intermediate tuned circuit F. The e.m.f. across a measured

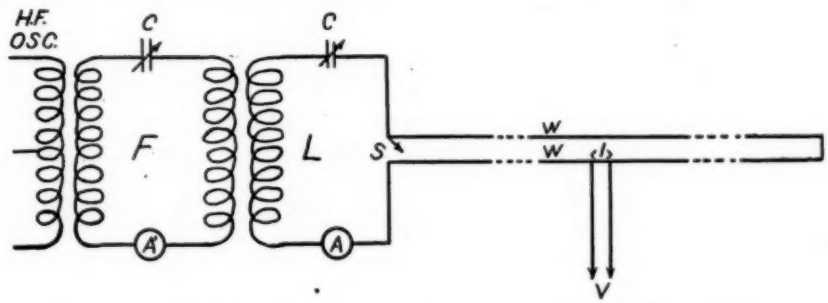

Fig. 3. Diagram of circuit for measuring the inductance of a short section of a straight wire.

length of one of the wires was measured by the voltmeter V, while the current through it was indicated by the ammeter A. The wave-length was determined by means of a wave meter. A few typical measurements by this method are shown in (a), Table V.

The total inductance of the wires WW was then determined in the following manner. With the switch S open, the circuit was tuned to resonance, the ammeter and voltmeter both serving to indicate resonance, and the capacity C_1 of the condenser C was observed. This was repeated with the switch S closed. If we represent the new condenser reading by C_2 and the total inductance of the wires by ΔL, then,

$$\Delta L = \left[\frac{\lambda}{1.884}\right]^2 \frac{C_2 - C_1}{C_1 C_2} \tag{1}$$

The value obtained by this method is shown in (b), Table V. The length, diameter, and spacing of the wires were carefully measured and the induc-

[3] Bureau of Standards Circular No. 74

tance calculated from these dimensions. The value thus obtained is shown in (c), Table V.

TABLE V

(a) *Measurement of a small inductance*

l	I	E	Inductance of l	Inductance per cm.
5 cm.	1 amp.	0.090 volts	0.0487 μh.	0.0097 μh.
10	1	0.172	0.0932	0.0093
15	1	0.260	0.141	0.0094
20	1	0.344	0.186	0.0093

Average inductance per cm. = 0.0094 μh.

(b) $C_2 = 2202\mu\mu f$; $C_1 = 1784\mu\mu f$; $\lambda = 1020$ meters.

ΔL(from Eq. 1.) = 31.2μh. Total length of wires = 3310 cm. Inductance per cm = 0.0094 μh.

(c) Length of rectangle = 1645 cm; Width of rectangle = 10 cm; Diameter for wire = 0.234 cm.

ΔL(calculated from dimensions) = 29.7μh. Inductance per cm = 0.0090μh.

MEASUREMENT OF A SMALL CAPACITY

The circuit shown in Fig. 4 may be used to determine capacities of the order of 1μμf. The condenser C is a low-loss variable air condenser capable of being read to 0.02μμf. The inductance L is made of large copper tubing. Thus, the circuit, having a very low resistance, may be very accurately tuned to resonance with the aid of the voltmeter V. Two wires WW about 125 cm long were connected to the terminals of the condenser and rigidly

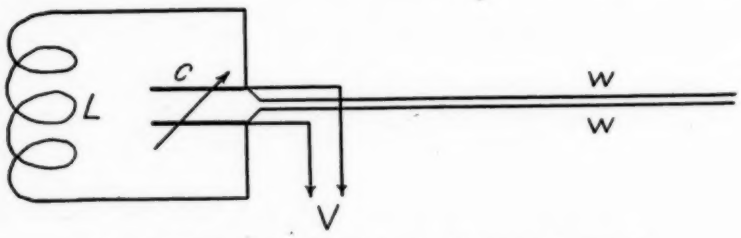

Fig. 4. Diagram of circuit for measuring a small capacity.

fixed parallel to one another. The circuit, very loosely coupled to an oscillator, was very accurately tuned to resonance, and the condenser read. A measured length of the wires was cut off, the circuit retuned, and the condenser again read. The capacity of the wires cut off was given, of course, by the difference of the condenser readings. The diameter of the wires and their distance apart were measured with micrometer calipers, and the capacity of the pieces cut off was calculated.[4] The results of these measurements are shown in Table VI.

[4] Bureau of Standards Circular No. 74.

TABLE VI

Measurement of capacity of two parallel wires. Wave length 143 *meters; diameter of wires* 0.203 *cm; distance between wires (center to center)* 0.447 *cm.*

Length of wire cut off	Observed capacity	Calculated capacity
4.4 cm.	0.85 μμf	0.83 μμf
5.8	1.10	1.09
10.2	1.95	1.91
29.5	5.51	5.53
49.9	10.35	10.38

Measurements of the capacity between the elements of vacuum tubes and the capacity of the socket terminals were made by this same method; and the results are shown in Table VII.

TABLE VII

Measurements of the capacity of vacuum tubes and sockets.

Type of tube	Filament to Plate capacity	Filament to Grid capacity	Grid to Plate capacity
201 A tube and socket	9.25 μμf.	8.5 μμf.	11.25 μμf.
Socket only	1.75	1.75	1.75
WD–11 tube and socket	5.00	5.00	3.60
Socket only	0.50.	0.50	0.25

MEASUREMENT OF THE IMPEDANCE OF A CONDENSER

The impedance of a paper telephone condenser was measured over a wide range of frequencies. The telephone condenser *C* (Fig. 5) was connected

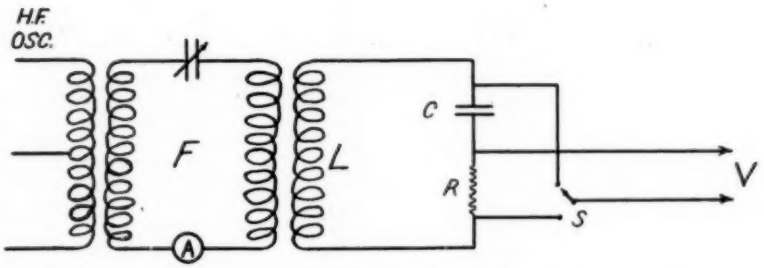

Fig. 5. Diagram for measuring the impedance of a fixed condenser at radio frequencies.

in series with a non-inductive standard resistance *R* and a coupling coil *L*. This circuit was coupled to an oscillator through the intermediate tuned circuit *F*. The voltmeter *V* was read with the switch *S* in positions 1 and 2,

respectively. Calling the corresponding electromotive forces E_e and E_R, the impedance Z, of the condenser C, is given by the relation,

$$Z = E_e/I, \quad \text{where} \quad I = E_R/R.$$

The construction of the condenser used is shown in Fig. 6, and the curves of Fig. 7 show impedance plotted against frequency for the three

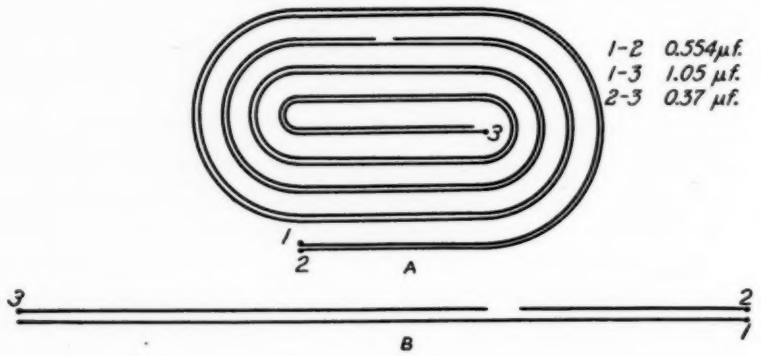

Fig. 6. Diagram showing the construction of the telephone condenser.

different sets of terminals corresponding to three different values of capacity. Table VIII shows data from which the curves were plotted. It will be noted

TABLE VIII

Impedance of paper telephone condensers.

Condenser	λ	E_e	I	Z
1.05 μf	2520 m.	0.332 v.	0.05 amp.	6.64 ohms
	4080	.146	.05	2.92
	4700	.118	.05	2.36
	5600	.0915	.05	1.83
	5975	.0880	.05	1.76
	6200	.0890	.05	1.78
	7200	.110	.05	2.20
	8000	.136	.05	2.72
	10000	.132	.03	4.40
0.37 μf	2000	.350	.05	7.00
	2860	.200	.05	4.00
	3000	.184	.05	3.68
	3100	.162	.05	3.24
	3300	.142	.05	2.84
	3400	.137	.05	2.74
	3500	.134	.05	2.68
	3550	.132	.05	2.64
	3600	.134	.05	2.68
	3750	.140	.05	2.80
	3850	.143	.05	2.86
	4100	.157	.05	3.14
	5150	.238	.05	4.68
0.554 μf	1000	.121	.100	1.21
	1800	.101	.05	2.02
	3150	.170	.05	3.40
	4120	.228	.05	4.56
	5070	.280	.05	5.60
	5975	.325	.05	6.50

that in two of the cases shown the inductance within the condenser was sufficient to cause the condenser to resonate at the frequency shown; whereas, in the third case, the curve shows no indication of resonance. An inspection of the diagram showing the construction of the condenser (Fig. 6) will suffice to make clear the reason for this difference.

The impedance of a variable standard air condenser of the Bureau of Standards type was measured at various settings by this method. The

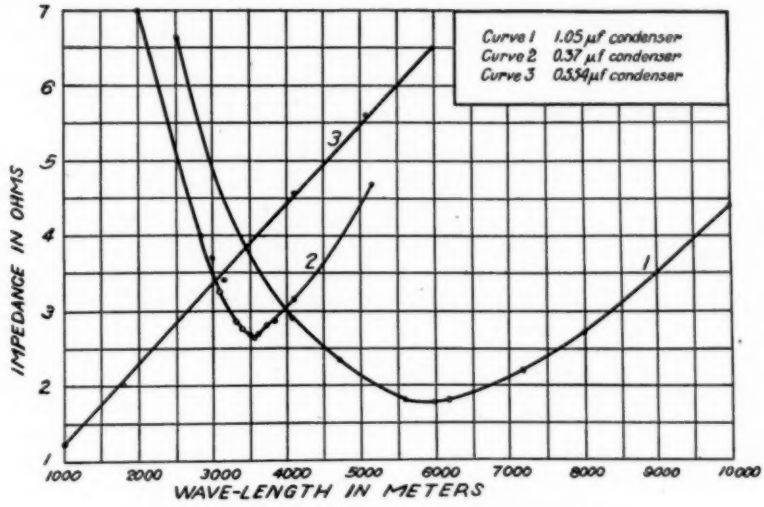

Fig. 7. Impedance curves for telephone condensers.

wave-length was determined by a wavemeter, and the corresponding values of capacity of the condenser were calculated from the measured values of its impedance. The results of this measurement are given in Table IX.

TABLE IX

Calibration of variable standard air condenser.
$\omega = 2\pi f = 8.73 \times 10^5$

Condenser Setting	I	E_c	$C\left(=\frac{I}{E\omega}\right)$	C (taken from Bureau of Standards calibration)
180	0.750 m.a.	0.218 v.	3940 μμf	3928 μμf.
175	.692	.205	3860	3866
170	.715	.218	3758	3760
160	.693	.223	3555	3542
150	.668	.228	3352	3324
140	.642	.237	3105	3107
130	.614	.242	2905	2890
120	.590	.248	2728	2673
110	.700	.328	2445	2455
100	.627	.319	2255	2236

The curve of Fig. 8 shows capacity plotted against setting, the crosses indicating values obtained by this method while the circles represent values taken from the calibration furnished by the Bureau of Standards.

It is believed that the methods described here will be found to have many applications in high frequency measurements. This paper will be followed

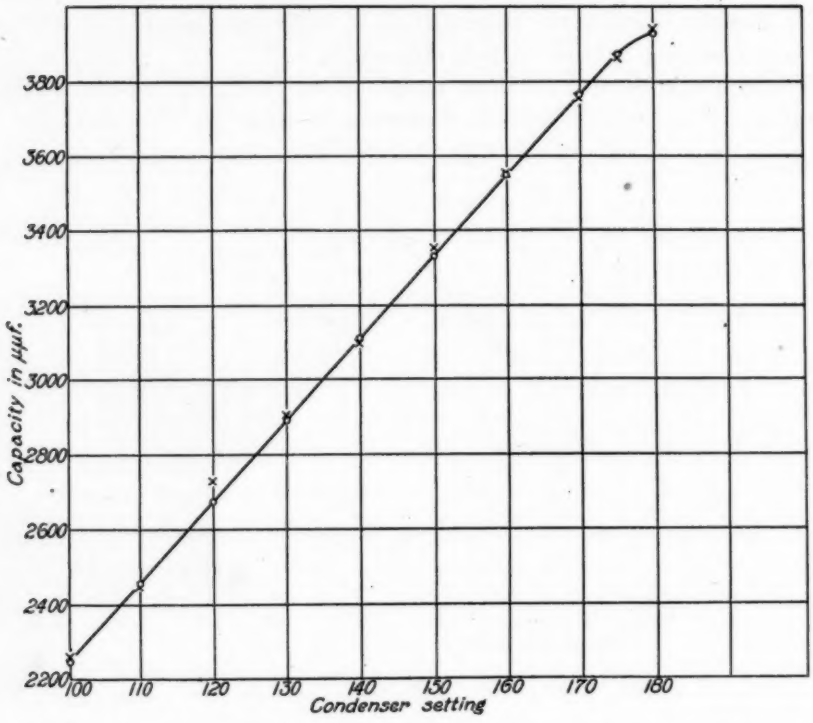

Fig. 8. Capacity of a standard condenser as determined from its measured impedance.

by one in which measurements of the resistance of low-loss variable air condensers are described. It will be shown that the resistance of the condenser in a low resistance circuit may be isolated.

HIGH FREQUENCY LABORATORY,
DEPARTMENT OF PHYSICS,
UNIVERSITY OF TEXAS.
February 15, 1927.

ON DIELECTRIC CONSTANTS AND MAGNETIC SUSCEPTIBILITIES IN THE NEW QUANTUM MECHANICS*

PART I.

A GENERAL PROOF OF THE LANGEVIN-DEBYE FORMULA

By J. H. Van Vleck

Abstract

In contradistinction to the old quantum theory, the new quantum mechanics yields very generally the Langevin and Debye formulas $\chi = N\alpha + N\mu^2/3kT$ for the magnetic and dielectric susceptibilities respectively. It is believed that our proof is considerably more comprehensive than previous ones, for it assumes only that the atom or molecule has a "permanent" vector moment of constant magnitude μ whose precession frequencies are small compared to kT/h. There is no limit to the allowable number of superposed precessions. There can, for instance, be simultaneous precessions due to internal spins of the electron and to "temperature rotation" of the nuclei. The presence of other simultaneous external fields in addition to the applied electric or magnetic field introduces no difficulty. Besides the effect due to the permanent moment, there is the term $N\alpha$ which arises from "high frequency" matrix elements associated with transitions from normal to excited states. This term is proved independent of the temperature. The susceptibility formula contains the factor 1/3 in the temperature term as generally as in the classical theory because of the high spectroscopic stability characteristic of the new quantum mechanics. It is shown that the mean squares of the x, y, and z components of a vector are equal in the new quantum dynamics just as in the classical theory, the only difference being that in the new quantum theory we take the average by summing over a discrete distribution of quantum-allowed orientations instead of by integrating over a uniform continuous distribution.

1. Introduction.

THE present paper is part I of a series of articles on magnetic and dielectric susceptibilities in the new quantum mechanics, and contains the main elements of the mathematical theory. Part II will discuss the application to dielectric constants, especially in relation to previous work by other authors with particular models. Part III will deal with applications to magnetism, including the paramagnetism of O_2 and NO.

The main purpose of part I is to give a very general derivation, also some critical discussion, of the Langevin-Debye formula

$$\chi = N\left(\alpha + \frac{\mu^2}{3kT}\right). \tag{1}$$

Here χ is the susceptibility, N is the number of atoms or molecules per unit volume, k is the gas constant, and α is a constant independent of the absolute

* Presented at the New York meeting of the American Physical Society, Feb. 1927.

temperature T. We shall suppose the susceptibility χ to be either magnetic or electric, not because of any deep physical resemblance of the magnetic and electric polarizations, but simply because it is well known that they can both be calculated by quite similar mathematical procedures, so that we shall treat them together wherever possible. Thus $1+4\pi\chi$ will denote the dielectric constant or magnetic permeability, and μ the permanent electric or permanent magnetic moment of the molecule, depending on whether we are dealing with electric or magnetic polarization. The interpretation of the constant α is somewhat different in the two cases; in the electric one α is the "induced moment" due to elastic polarization of the atom or molecule by the impressed field, while in the magnetic case α is usually negative and represents the induced diamagnetic moment, although we shall see in part III that the magnetic α is occasionally positive due to the quadratic Zeeman effect associated with multiplet structures. Thus in magnetism α is usually small, and so ordinarily omitted. Historically, Eq. (1) was first applied to magnetism, as in 1905 Langevin[1] published his famous paper, and it was not until 1912 that Debye[2] extended the formula to dielectric constants by assuming that there could be a "permanent" as well as "induced" electric moment in polar molecules.

Our derivation of (1) will be based on the new quantum mechanics. There is, however, an interesting analogy with the classical theory, as it will be shown in part II that the same result could be obtained classically if we averaged continuously over all possible orientations of the moment and precession vectors relative to each other and to the field instead of summing over the discrete quantum states. It must be regarded as one of the triumphs of the new quantum mechanics that it will give the Langevin or Debye formulas very generally, whereas the old quantum theory replaced the factor $\frac{1}{3}$ in (1) by a constant C whose numerical value depended rather chaotically on the type of model employed, whether whole or half quanta were used, whether there was "weak" or "strong" spacial quantization, etc.[3] This replacement of $\frac{1}{3}$ by C caused an unreasonable discrepancy with the classical theory at high temperatures, and in some instances the constant C even had the wrong sign.[4] All these vicissitudes in C are avoided in the new mechanics, which gives the factor $\frac{1}{3}$ quite as generally as the classical theory. This

[1] P. Langevin, Journal de Physique, (4), **4**, 678 (1905); Annales de Chim. et Phys. (8), **5**, 70 (1905).

[2] P. Debye, Phys. Zeits. **13**, 97 (1912). See also his excellent compendium on electric and magnetic polarizations in vol. VI of the Handbuch der Radiologie. The temperature effect due to permanent dipoles was also suggested later independently by J. J. Thomson, Phil. Mag. **27**, 757 (1914).

[3] Cf. W. Pauli, Jr., Zeits. f. Physik, **6**, 319 (1921); L. Pauling, Phys. Rev. **27**, 568 (1926).

[4] Pauling[3] shows that C would be negative in molecules of the HCl type if we use the a-priori probability $2m$ indicated by the recent band spectrum intensity measurements of Bourgin and Kemble. He therefore uses a probability $2m+1$ and finds C to be about 14 times the classical value 1/3, but in a later paper[5] shows that C would even then become negative in the formula for the dielectric constant on applying a magnetic field at right angles to the electric field. Needless to say, such a behavior is not found experimentally.

has already been shown by several writers[5] for special models, and the present paper may be regarded as extending the result to the general case. In our opinion the general proof is usually quite as simple as the specialized ones with particular models, since the algebra of writing out and summing the various matrix elements is avoided, and there is the great advantage that it is unnecessary to know the precise form or values of these elements.

At this point it may be remarked that most of the classical derivations of (1) appear rather inadequate. The literature, to be sure, is full of purported "generalized Langevin theories,"[6] but these for the most part are based on rather unsatisfactory physical premises, such as rigid magnetons, steady molecular currents, etc. The usual elementary derivation of the Langevin formula omits even the kinetic energy of rotation. Fortunately the calculations of Alexandrow[7] and van Leeuwen[8] show that the inclusion of this energy occasions no particular difficulty in symmetrical diatomic molecules. Miss van Leeuwen replaces an electron orbit by a current, but unlike most writers, she does not overlook the gyroscopic effect arising from the angular momentum concomitant to magnetic moment. No computations, however, appear to have previously been published which allow for the high degree of dissymmetry characteristic of the general polyatomic molecule, or for the precessions caused by internal spins[9] of the electrons which are an important factor in magnetism. Thus the following treatment not only substitutes the new quantum for the classical viewpoint, but also gives increased generality. Yet it must be understood that we shall calculate only the terms in the susceptibility which are independent of the field strength. These are the only terms ordinarily of consequence in dielectric or in para- (or dia-) magnetic media, but the present paper does not pretend to treat ferromagnetism or saturation phenomena in which higher powers of the field F must be considered. Hence we have written Langevin's formula in its asymptotic form (1) valid for small (i.e. ordinary) values of the field rather than giving his more complete expression which contains the effect of all powers of $\mu F/kT$. We suppose throughout for simplicity that the effective average field on the atom is F rather than the more rigourous expression $F+4\pi P/3$. This amounts to assuming the polarization so small that the Clausius-Mosotti constant $(\epsilon-1)/(\epsilon+2)N$ reduces to $(\epsilon-1)/3N$; if this condition is not met there is no trouble, as we would simply have to replace χ in (1) by $3\chi/(3+4\pi\chi)$.

[5] L. Mensing and W. Pauli, Jr., Phys. Zeits. **27**, 509 (1926); J. H. Van Vleck, Nature, **118**, 226 (1926); R. d. L. Kronig, Proc. Nat. Acad. **12**, 488, 608 (1926); C. Manneback, Phys. Zeits. **27**, 563 (1926); P. Debye and C. Manneback, Nature, **119**, 83 (1927); L. Pauling, Phys. Rev. **29**, 145 (1927).

[6] For references see "Theories of Magnetism," Bull. Nat. Research Coun. no. 18; also van Leeuwen.[8]

[7] W. Alexandrow, Phys. Zeits. **22**, 258 (1921).

[8] van Leeuwen, Leyden Thesis; summary in J. de Physique, (6), **2**, 361 (1921).

[9] We assume the reader to be familiar with the Uhlenbeck-Goudsmit spinning electron, die Naturwissenschaften **13**, 953 (1925); Nature **117**, p. 264 (1926).

2. The Fundamental Assumptions

In order to derive the second term of (1) *we find it necessary to assume only that the atom or molecule has a "permanent" moment vector whose precession frequencies are small compared to* kT. Another way of saying the same thing is that the various component normal states have a vector moment of common magnitude μ, and have an energy spacing small compared to the equipartition allowance kT. A more precise explanation of these conditions is given in the following paragraphs.

The stationary states of many atoms and molecules are so spaced that at ordinary temperatures there is a fairly sharp delineation between normal and excited states. The excited states we define as having energies of excitation which are large in comparison with kT, and so they may be considered as virtually unoccupied in making the calculations. The normal states generally are a family of "component" energy levels whose separation is usually smaller than or comparable with kT. This splitting into components ordinarily results from the mutual precessions of the various constituent angular momentum vectors of the atom or molecule and from the precession of their resultant about some direction fixed in spaced. Thus the excited states are usually characterized by different electronic or possibly vibrational quantum numbers from the normal, whereas the component normal levels result from giving the molecules different amounts of "temperature rotation," different orientations relative to the external fields, or from allowing the spin axis of the electron to assume different orientations relative to the rest of the system.

It is clear that the magnetic or electric moment of the atom or molecule is a vector matrix $\mathbf{M}$. We follow Born's procedure of writing matrices in bold-face type. Certain elements of the matrix $\mathbf{M}$ will be identified with transitions between normal and excited states, and will be shown in section 3 to contribute only to the constant term $N\alpha$ in (1) which is independent of the temperature; even without proof this seems fairly obvious from the fact that excited states have by definition energies large compared with kT. Hence to calculate the second or "temperature" term of (1) we replace $\mathbf{M}$ by a matrix $\boldsymbol{\mu}$ formed from $\mathbf{M}$ by dropping the high frequency elements of $\mathbf{M}$ associated with transitions to excited states. This replacement of $\mathbf{M}$ by $\boldsymbol{\mu}$ corresponds to the well-known separation of the "secular" from the high frequency variations in perturbation theory, and means that in computing the temperature effect the moment matrix may be considered to involve just the family of normal states rather than the more complicated aggregate of both normal and excited states. We suppose, moreover, that the atom (or molecule) has a moment of "definite" or "permanent" magnitude μ. This is not at all a drastic assumption, as it is involved in all permanent dipole theories, and without it the expression μ in (1) would have no meaning. This means that the magnitude $\mu=(\boldsymbol{\mu}_x^2+\boldsymbol{\mu}_y^2+\boldsymbol{\mu}_z^2)^{1/2}$ of the vector matrix $\boldsymbol{\mu}$ is constant with respect to the time and the same for the various normal states. Hence $|\boldsymbol{\mu}|$ is a diagonal matrix whose elements are all equal and in the terminology of Dirac it may be called a "c-number," which is the moment μ entering in Eq. (1). The vector $\boldsymbol{\mu}$ will be constant in magnitude but usually

not in direction. The components $\mathfrak{y}_x$, $\mathfrak{y}_y$, $\mathfrak{y}_z$ will, to be sure, involve no high frequency elements, as the latter have been eliminated in forming $\mathfrak{y}$ from **M**, but these components will in general vary with the time due to the existence of "low frequency elements" which correspond to transitions between the different levels constituting the normal states and which arise usually from precessions of the various types cited in the preceding paragraph. In order to obtain the Langevin formula (1) it is essential simply that these "low frequencies" be small in comparison with kT/h, which is equivalent to saying that transitions between the various normal states involve energy changes of magnitude much less than kT.

In the above and elsewhere we use the terms, "direction of a vector," "precession," etc., rather freely, as a vector matrix clearly cannot be assigned the same simple geometrical interpretation as an ordinary directed segment. We mean, of course, simply the quantities in the Born-Heisenberg matrix theory which "correspond" to the precessions, directions, etc., of classical mechanics. In particular the precession frequencies mean the spectroscopic frequencies emitted or absorbed in transitions between various component levels whose separation is caused by the quantum analog of a classical precession effect. Throughout the present paper, and also in parts II and III, we use the language of the matrix rather than wave form of the new quantum mechanics, but the same results follow equally well with the wave viewpoint, in virtue of the general formal identity[10] of the wave and matrix formulations for closed ("abgeschlossen") atomic systems. In fact we could even obtain the Langevin formula by going to the opposite extreme from the matrix aspect, and employing the "field" theory of Schroedinger, Madelung, and Gordon,[11] in which the electric charges are spread through space with a continuous density proportional to $|\psi|^2$, where ψ is the well-known Schroedinger wave-function. The identity of the results regarding susceptibilities ensues since Schroedinger[10] has shown that the field theory gives the same electrical moment as the matrix viewpoint (neglecting relativity corrections), while Fermi[12] has proved it gives the same magnetic moment,[13] utilizing the definition of the velocity of flow given by Schroedinger and others.[14]

[10] E. Schroedinger, Ann. der Physik, **79**, 734 (1926); C. Eckhart, Phys. Rev. **28**, 711 (1926).

[11] E. Schroedinger, Ann. der Physik, **81**, 109 (1926) **82**, 257, 265 (1927); E. Madelung, Naturwissenschaften, **14**, 1004 (1926); Zeits. f. Physik, **40**, 322 (1926); W. Gordon, *ibid.*, **40**, 117 (1926).

[12] Fermi, Nature, **118**, 876 (1926).

[13] It must be remarked, however, that calculations similar to Fermi's establish the similarity of results for the part of the paramagnetism arising from orbital angular momentum, and do not indicate just how to treat the "spin" phenomenon, as Fermi assumes the normal ratio of magnetic moment to angular momentum holds throughout. A further complication is that diamagnetism involves the velocity of light to the power $1/c^2$ rather than $1/c$, and the ordinary technique does not furnish a correlation to $1/c^2$, as the magnetic modifications in the definition of momenta, etc., would have to be considered, so that there is a bare possibility of a discrepancy. It seems, however, highly improbable that any successful theory will give different susceptibilities than those calculated by the matrix method.

[14] For references see note 11.

The basic assumptions may be summarized in the words "permanence of moment" and "slowness of precession." The great generality arises from the fact that it is not necessary to specify the exact form of the precession, or the numerical formulas for the frequencies and amplitudes. The phrase "slowness of precession" must not be construed too literally, for the low frequency elements could result equally well from slow oscillations or other types of motion than precessions. We use the term "precession" for the sake of concreteness and because precessions are much the most common cause of low frequency components; "temperature rotation" of the nuclei about the center of gravity, for instance, can be considered as simply a precession about the invariable axis. It is also to be understood that besides the "low frequency elements" there are generally high frequency terms which are responsible for the constant term $N\alpha$ in (1). The essential requirement, of course, is that the "high" and "low" frequencies be always respectively large and small compared to kT/h. An important feature is that there is no limit to the number of precessions which can be superposed. Nevertheless, even our hypotheses are not sufficiently general in some instances. In the first place, in the case of dielectric constants, the centrifugal expansion of the molecule will violate the assumption of a "permanent electric moment," as the stretching will slightly increase the dipole moment in the higher quantum states, so that the diagonal elements of the matrix $|\mu|$ are no longer equal. Fortunately this expansion effect is small, as band spectra show that the variation of moment of inertia with rotation rarely exceeds six per cent even in the more elastic excited states.[15] A more important restriction is imposed by the requirement that the elements in the moment matrix $\mathbf{M}$ are all of the "high" or "low" frequency type. Actually Laporte and Sommerfeld[16] find that in atoms of the first long period of the Mendeleeff table the internal spins of the electron lead to precessions in the magnetic moment of what we may term the "medium" frequency type; i.e., precessions whose frequencies are of the same order of magnitude as kT/h. We shall find it necessary to treat the magnetism of NO by a special calculation in part III because the spacing of its spin doublet is about $.6kT/h$. Also the variable vibrational specific heats of certain molecules indicate that the energies of excitation of their nuclear vibrations are comparable with kT. Undoubtedly because of its secular character the magnetic moment does not have any terms of appreciable amplitude involving the vibrational frequencies. The electric moment will contain such terms, but fortunately their temperature effect will be very subordinate since the amplitude of nuclear vibration is usually small compared to the equilibrium nuclear spacing, and also since the polarization of a linear oscillator, which represents the nuclear vibrations to a first approximation, is independent of the temperature.[17]

[15] Cf. R. T. Birge, Nature, **116**, 783 (1925).

[16] Laporte and Sommerfeld, Zeits. f. Physik, **40**, 333 (1926).

[17] This independence of the temperature for the polarization due to a linear oscillator is proved with the classical theory by P. Debye, Handbuch der Radiologie, Vol. VI, p. 613, and a simple calculation shows that it also holds in the new quantum mechanics.

3. Proof

Let us suppose for simplicity that we are dealing with electric rather than magnetic polarization. The slight adaptations in the proof necessary to the magnetic case will be given in part III. Before application of the field F the electrical moment $\mathbf{M}$ will be a matrix whose typical element may be denoted by

$$M_z(njm\ ;\ n'j'm')e^{2\pi i\nu(njm;n'j'm')t}$$

We have here taken the z-component, but there are, of course, similar formulas for the x and y components. For brevity we throughout omit commas from the arguments, and write $(njm;\ n'j'm')$ for $(n,\ j,\ m;\ n',\ j',\ m')$, etc. Following the conventional notation, such an element is associated with a transition from a state specified by indices $n,\ j,\ m$ to one by $n',\ j',\ m'$. We shall let the first of the three indices be identified with quantum numbers (e.g. "electronic" and "vibrational") which have an effect on the energy large compared to kT, so that one particular value of this index gives states of especially low energy. This value will be denoted by n and yields the normal levels of the atom or molecule. The second index j or j' corresponds to quantum numbers (e.g. "inner," "rotational," "spin") whose effect on the energy is comparable with or smaller than kT. We do not, however, include in the second index the "axial" (also called "equatorial" or "magnetic") quantum number which specifies the spacial orientation by quantizing angular momentum about some fixed direction in space. Instead the third index m or m' is to be considered as representing the axial quantum number. Thus the various component levels of the normal state correspond to fixed n but different values of j and m, whereas the excited states have an index n' different from n. It is clearly to be understood that *each index, except the third, in general symbolizes more than one quantum number*; i. e., represents a multiple rather than single array. Hence we designate $n,\ j,\ m$ as "indices" rather than quantum numbers. Our proof is thus by no means confined to systems with three quantum numbers or degrees of freedom.

Let us suppose an electric field F is applied in the z-direction. The susceptibility is the quotient of polarization by field strength, or $N\overline{M}_z^{(F)}/F$, where N is the number of molecules (or atoms) per unit volume, and $\overline{M}_z^{(F)}$ is the average value of the z-component of the electrical moment per molecule. This average, of course, differs from the time mean[18] $M_z^{(F)}\ (njm;\ njm)$ for individual molecules, as the latter will be distributed among the different components of the normal levels. To get $\overline{M}_z^{(F)}$ we must average over these components with each assigned the probability required by the Boltzmann distribution formula. Hence it is apparent that

[18] The time mean value in a non-degenerate system is a diagonal term of a matrix, and hence specified by an element in which the second trio of indices is the same as the first. In defining this time mean it is, of course, supposed that the molecule always remains in the same state. Thus the time mean is over a period long compared to the periods of the spectral lines but short compared to the duration of a stationary state. Heisenberg's statistics of fluctuations (Zeits. f. Physik, **40**, 501, 1926) shows that (2) is still applicable even if we allow for a molecule changing states.

$$\chi=\frac{N}{F}\,\frac{\sum_{j,m} M_z^{(F)}(njm\,;\,njm)e^{-W^{(F)}(njm)/kT}}{\sum_{j,m} e^{-W^{(F)}(njm)/kT}}, \tag{2}$$

where W as usual denotes the energy. We suppose the system non-degenerate,[19] so that all states have the same statistical weight; i.e. the same factor g in the Boltzmann expression $ge^{-W/kT}$.

Because of "induced polarization," the time mean $M_z^{(F)}$ $(njm;\ njm)$ of the electrical moment in the field F is not the same as this mean $M_z(njm;\ njm)$ before application of F. We shall throughout use the superscript $^{(F)}$ to distinguish values in the field from those in its absence. It is clearly to be understood that all amplitudes, frequencies, and energies without this superscript relate to the case $F=0$. Now $M^{(F)}$ is easily calculated in terms of M by the perturbation methods of Born, Heisenberg, and Jordan,[20] or of Schroedinger.[21] These writers show that [22]

$$M_z^{(F)}(njm\,;\,njm)=M_z(njm\,;\,njm)-\frac{2F}{h}\sum{}'_{n'\,j'\,m'}\frac{|\,M_z(njm\,;\,n'j'm')\,|^2}{\nu(njm\,;\,n'j'm')}. \tag{3}$$

This is, of course, the same result as given by extrapolation of the Kramers dispersion formula to infinitely long impressed wave-lengths. The sum over n', j', m' includes all excited and normal states except the given state n, j, m. This exclusion of the one term $n', j', m'=n, j, m$ is indicated by the prime inside the summation sign, and this interpretation of the prime is to be understood throughout the article. As usual ν denotes the frequency emitted (or absorbed) in the transition between two states when $F=0$. Eq. (3) is utilized by all the various writers[5] who have calculated dielectric constants for particular models. It gives the polarization to terms of the first order in F, as this degree of approximation is necessary to get the ordinary susceptibility effects (cf. section 1).

Now the energy in the field is to first powers in F

$$W^{(F)}\,(njm)=W(njm)-FM_z(njm;\,njm). \tag{4}$$

This follows by well-known perturbation formulas of the new quantum mechanics,[20] which show that here just as in the old quantum theory the perturbed energy is to a first approximation the energy $W(njm)$ in the absence of F augmented by the perturbative potential (here $-FM_z$) averaged over the unperturbed motion.

[19] In case the system is degenerate, we may imagine the degeneracy removed by introducing a sufficient number of hypothetical supplementary infinitesmal internal forces. This is legitimate, as Eq. (25) of section 4 shows that the result is invariant of the manner in which the degeneracy is removed. There can be no spacial degeneracy, for the field F provides an axis for quantization if not already present when $F=0$.

[20] Born, Heisenberg, and Jordan, Zeits. f. Physik, **35**, 567 (1927).

[21] E. Schroedinger, Ann. der Physik, **81**, 109 (1926).

[22] Expressions of the type form $|\,M_z(njm;n'j'm')\,|^2$ occurring in Eq. (3) etc. may also be written as the product $M_z(njm;n'j'm')\,M_z(n'j'm';njm)$; for as the moment matrix is Hermitian, $M_z(n'j'm';njm)$ is the conjugate of $M_z(njm;n'j'm')$, and the product of any complex number and its conjugate is the square of its absolute value. This other method of writing is that used by Born, Heisenberg, and Jordan.[20]

We now expand the exponentials in (2) as power series in F by means of (4). When we do this and substitute (3) in (2) we find

$$\chi=\frac{N}{F}\frac{\sum_{j,m} M_z(njm\,;\,njm)e^{-W(njm)/kT}}{\sum_{j,m} e^{-W(F)(njm)/kT}}$$
$$+(B/kT)\sum_{j,m}\left|M_z(njm\,;\,njm)\right|^2 e^{-W(njm)/kT} \qquad (5)$$
$$-\frac{2B}{h}\sum{}'_{j,m,n',j',m'}\frac{\left|M_z(njm\,;\,n'j'm')\right|^2 e^{-W(njm)/kT}}{\nu(njm\,;\,n'j'm')}.$$

Here we have discarded terms in F, F^2, $\cdots$, as we are interested in calculating only the constant part of the susceptibility. We have written $|M_z(njm;\,njm)|^2$ for $M_z(njm;\,njm)^2$ which is legitimate since diagonal elements are real. Also we have introduced the abbreviation

$$B=\frac{N}{\sum_{j,m} e^{-W(njm)/kT}}. \qquad (6)$$

We must now suppose that the first line of (5) vanishes. (For this reason we have not bothered to expand the exponentials in the denominator of this line.) This involves no essential loss of generality,[23] for if it did not we would have a "permanent" or "residual" polarization even in the absence of the field.[24] Clearly the numerator of the first line of (5) vanishes by symmetry if the only external field is the applied electric field F, for in the absence of all fields there can be no preference between directions parallel and antiparallel to F, and hence no moment along F; another way of saying the same thing is that in the absence of all fields states with positive and negative values of the axial quantum number are equally probable. In solids there is, of course, the possibility of directed[25] inter-molecular fields, which might give the body a residual polarization when $F=0$, but such effects are not ordinarily found experimentally except in ferromagnetic media or in crystalline dielectrics, both of which are beyond the scope of the present article.

Separation of high and low frequency terms. Eq. (5) is a perfectly general expression for the susceptibility which does not require the hypotheses of "slowness of precession" or "permanent dipole moment" presented in section 2. For further simplification, however, these postulates must be introduced, and so we now proceed to make the separation into "low" and "high" frequency terms. In order to make connection with the notation employed in section 2, we write $\mu(jm;\,j'm')$ for the low frequency elements $M_z(njm;\,nj'm')$. Eq. (5), with first line omitted, then becomes

[23] Debye also notes (Phys. Zeits. **27**, 67, 1926) in a calculation with the old quantum theory that the vanishing of an expression similar to the first line of (5) involves no essential loss of generality.

[24] The first line of (5) will not vanish if there is a "magneto-electric directive effect", to be explained in part II, but this effect is apparently never found experimentally.

[25] Random inter-molecular fields give no trouble, as with them the first line of (5) vanishes on the average by symmetry.

$$\chi=(B/kT)\sum_{j,m}|\mu_z(jm\,;jm)|^2\,e^{-W(njm)/kT}$$
$$-\frac{2B}{h}\sum{}'_{j,m,j',m'}\frac{|\mu_z(jm\,;j'm')|^2\,e^{-W(njm)/kT}}{\nu(njm\,;nj'm')} \tag{7}$$
$$-\frac{2B}{h}\sum{}_{j,m,n',j',m',\,(n'\neq n)}\frac{|M_z(njm\,;n'j'm')|^2}{\nu(njm\,;n'j'm')}e^{-W(njm)/kT}.$$

Here the first two and the third lines represent respectively the "low" and "high" frequency terms, as the third line involves only terms associated with transitions to the excited states $n'\neq n$.

The terms in the summation in the second line of (7) may be grouped together in pairs P_{12} of the form

$$P_{12}=-\frac{2B}{h}\left\{\frac{|\mu_z(j_1m_1\,;j_2m_2)|^2}{\nu(nj_1m_1\,;nj_2m_2)}\,e^{-W(nj_1m_1)/kT}\right.$$
$$\left.+\frac{|\mu_z(j_2m_2\,;j_1m_1)|^2}{\nu(nj_2m_2\,;nj_1m_1)}\,e^{-W(nj_2m_2)/kT}\right\}. \tag{8}$$

Now $\mu_z(j_2m_2;\,j_1m_1)$ is the conjugate of $\mu_z(j_1m_1;\,j_2m_2)$ and so has the same absolute magnitude. Also $\nu(nj_2m_2;\,nj_1m_1)=-\nu(nj_1m_1;\,nj_2m_2)$, and by the Bohr frequency condition $W(nj_2m_2)=W(nj_1m_1)-h\nu(nj_1m_1;\,nj_2m_2)$. Under the hypothesis of "slowness of precession," fully explained in section 2, we may develop the second exponential in (8) as a power series in the ratio $s=h\nu(nj_1m_1;\,nj_2m_2)/kT$. Then (8) becomes

$$P_{12}=-2(B/skT)\,|\mu_z(j_1m_1\,;j_2m_2)|^2\,e^{-W(nj_1m_1)/kT}[1-1-s-\tfrac{1}{2}s^2-\tfrac{1}{6}s^3-\cdots] \tag{9}$$

If we neglect terms of the order s^3 within the bracketed factor this is the same as

$$P_{12}=(B/kT)\left\{|\mu_z(j_1m_1\,;j_2m_2)|^2\,e^{-W(nj_1m_1)/kT}+|\mu_z(j_2m_2;\,j_1m_1)|^2\,e^{-W(nj_2m_2)/kT}\right\} \tag{10}$$

Now if the influence of orientation, i.e., of the axial quantum number, on the "unperturbed" energy $W(njm)$ is small compared to kT, we may replace $W(njm)/kT$ by an expression $W(nj)/kT$ independent of the index m. This approximation is usually one which is fulfilled with a high degree of precision. In the first place the ordinary case is that in which the molecule is subject to no external field except F, and then the unperturbed energy (i.e., the energy in the absence of F) is independent of orientation, so that the index m has absolutely no effect on W. To allow for the possibility of simultaneous electric and magnetic fields, or weak inter-molecular fields in liquids and solids, we admit the more general assumption that $W(njm)-W(nj)$ is not identically zero but small compared to kT.[26] Also it is clear that the

[26] It is to be noted that though we suppose $W(njm)-W(nj)$ and $h\nu(njm;nj'm')$ both numerically small compared to kT, we have not assumed that $W(njm)-W(nj'm')$ is negligible relative to kT. The latter assumption would be much more stringent, for usually there are selection principles which require that certain quantum numbers change only by zero or one unit, at least in the transitions of appreciable amplitude. In case the quantum numbers

"high" frequencies $\nu(njm; n'j'm')$ $(n' \neq n)$ are affected but little by the indices j, m, j', m', as the separations between components of the normal states or of the excited states are small compared to the interval between the normal and excited states. Hence in the third line or "high frequency part" of (7) we may without appreciable error replace $\nu(njm; n'j'm')$ by a number $\nu(n; n')$ independent of the indices j, m, j', m'.

If we use the simplifications given in the preceding paragraph, and substitute (10) for (8), Eq. (7) reduces to

$$\chi = (B/kT) \sum_{j,m,j',m'} | \mu_z(jm\ ;\ j'm') |^2\ e^{-W(nj)/kT} - \frac{2B}{h} \sum_{j,m,n',j',m'(n' \neq n)} \frac{| M_z(njm\ ;\ n'j'm') |^2}{\nu(n\ ;\ n')} e^{-W(nj)/kT}, \tag{11}$$

where now the first sum includes the diagonal elements $n', j', m' = n, j, m$.

It will be proved in section 4 that in virtue of the high degree of spectroscopic stability characteristic of the new quantum mechanics, an expression of the form

$$\sum_{m,m'} | A_z(njm\ ;\ n'j'm') |^2$$

is invariant of the direction of the axis of spacial quantization and equals

$$\tfrac{1}{3} \sum_{m,m'} | A(njm\ ;\ n'j'm')^2, |$$

Here $A(njm; n'j'm')$ denotes an element of the scalar magnitude $|\mathbf{A}| = (\mathbf{A}_x^2 + \mathbf{A}_y^2 + \mathbf{A}_z^2)^{1/2}$ of a vector matrix $\mathbf{A}$ whose z-component has elements of the form $A_z(njm; n'j'm')$. This consequence of spectroscopic stability is perhaps the most interesting and vital feature of the entire proof, as it underlies the general occurrence of the factor $\frac{1}{3}$ in the temperature term of the Langevin-Debye formula. On taking $A = M$ $(n' \neq n)$ and $A = \mu$ $(n' = n)$ (this is only a difference in notation) Eq. (11) becomes by the above

$$\chi = (B/3kT) \sum_{j,m,j',m'} | \mu(jm; j'm') |^2\ e^{-W(nj)/kT} - \frac{2B}{3h} \sum_{j,m,n',j',m'(n' \neq n)} \frac{| M(njm\ ;\ n'j'm') |^2}{\nu(n\ ;\ n')} e^{-W(nj)/kT} \tag{12}$$

---

associated with the index j can assume a wide range of values, this means that $h\nu(njm;nj'm')$ is considerably smaller in magnitude than the general expression of the form $W(njm) - W(nj'm')$ for then the selection principle requires that $h\nu(njm;nj'm')$ equal the difference of two adjacent, or nearly adjacent components of the normal levels rather than of two comparatively widely separated such levels.

This fact explains why we can apply our proof of the Langevin-Debye formula to molecules having "temperature rotation" even though by giving the molecule sufficient quanta of rotation the ratio $s = h\nu(njm;nj'm')/kT$ may be made as large as we please. For the numerical magnitude of the exponent in the Boltzmann distribution factor $e^{-W(nj)/kT}$ increases much more rapidly than s. (One varies approximately as the square, the other as the first power of the rotational quantum number.) Hence terms for which s is comparable with unity will have such a small exponential factor or probability that they can be disregarded. This will be discussed more fully in part II, where a calculation will be made of the error due to neglecting higher powers of s in (9).

Simplification of low frequency elements. From the rules for matrix multiplication it follows that

$$\sum_{j',m'} \left| \mu(jm\,;j'm') \right|^2 \tag{13}$$

is a diagonal element $\mu^2(jm;jm)$ of the matrix $\mathfrak{y}^2$, which is the square of the absolute magnitude of the secular moment vector matrix $\mathfrak{y}$ formed from $\mathbf{M}$ by deleting the high frequency elements (cf. p. 730). Now in consequence of the hypothesis of a "permanent dipole moment," fully explained in section 2, the magnitude of $\mathfrak{y}^2$ is independent of the time and the same for all the component levels constituting the normal state. Hence $\mu^2(jm;jm)$ is a number μ^2 independent of j and m, so that the expression (13) reduces to μ^2 and the low frequency part (first line) of (12) now becomes

$$(B/3kT)\mu^2 \sum_{j,m} e^{-W(nj)/kT}. \tag{14}$$

Now we have already supposed on p. 736 that $W(njm)$ can be replaced by $W(nj)$ in the exponential factors, so that the denominator of (6) is identical with the sum[27] in (14). Hence by (6) Eq. (14) is simply $N\mu^2/3kT$, which is the "temperature part" of the Langevin-Debye formula.

Invariance of high frequency part of χ. The high frequency terms, represented by the second line of (12), are not included in the ordinary calculations of molecular susceptibilities or dielectric constants, and instead it is usually taken for granted, perhaps by analogy with a classical linear oscillator,[17] that their net effect is invariant of the temperature. The warrant for this seems to the author by no means so obvious but what it is repaying to actually demonstrate that the total contribution of the high frequency elements is independent of T. The analysis has, of course, been somewhat lengthened by their inclusion but gains considerably in completeness. The demonstration is an easy consequence of the "sum-rules" for intensities applied to absorption rather than emission, for it is the essence of these rules that an expression[28] of the form

$$\sum_{j'm'} \left| M(njm\,;n'j'm') \right|^2 \tag{15}$$

is independent of the indices j and m, provided the spacing of components is small compared to the frequency of the line itself; i.e., provided $\nu(njm;n'j'm')$ can be replaced by $\nu(n;n')$ as already assumed on p. 737. The sum-rules were first established on semi-empirical grounds, but the work of

[27] The double sum in (14) may also be written as the single summation $\sum_j p_j e^{-W(nj)/kT}$ where p_j is the number of quantum-allowed orientations for the state j; i.e., the number of permissible values for the axial quantum number. The expression p_j would be the a-priori probability if the spacial degree of freedom were neglected and the system consequently treated as degenerate. Ordinarily p_j-1 equals twice the maximum value of the axial quantum number, as positive and negative values of this number are equally probable.

[28] As usually stated, the sum-rules relate to the invariance of intensity, and intensity is proportional to the fourth power of the frequency as well as to the resultant amplitude M^2 which represents the combined effects of the x, y, and z components. However, we have seen that $\nu(njm;n'j'm')$ can without sensible error be replaced by an expression $\nu(n;n')$ independent of j,m,j',m', and so the independence of the intensity-sums of j and m also implies the independence of (15) of j and m.

Born, Heisenberg, and Jordan,[29] and of Dirac[30] shows that they are required by the new quantum mechanics.[31] The ordinary sum-rule for Zeeman components shows that $\sum_{m'}|M(njm;\,n'j'm')|^2$ is independent of m, and this taken in conjunction with the sum-rule for "multiplet" components[32] (or band spectrum components) shows that (15) is independent of both j and m, at least provided j is associated with the one type of precession ordinarily identified with the inner (or rotational) quantum number. Actually we have already stated that the index j may correspond to several quantum numbers and hence represent the effect of several superposed precessions; e.g. simultaneous precessions resulting from internal spins of the electrons and from "temperature rotation." However, Dirac notes on p. 298 of his paper[30] that there is no difficulty extending the proof of the intensity rules to systems which are composed of any number of parts and which so contain any number of precessions, provided the parts are coupled together by "secular" forces which do not distort the motion and instead give rise only to pure precession. This result is also obvious from the correspondence principle inasmuch as the sum-rule is the quantum analog of the fact that classically the intensity of radiation is not appreciably affected by slow precessions which do not sensibly alter the sizes and shapes of the orbits. It must, however, be emphasized that the validity of the sum-rule requires that the coupling responsible for the separation of the normal levels into components must result in "pure precession" without distortion. This rules out centrifugal expansion and similar effects, but we have already seen at the close of section 2 that their effect is only subordinate.

From what has been said in the preceding paragraph we may replace (15) by an expression $|M(n;\,n')|^2$ independent of j and m, and so the second line of (12) reduces to

$$-\frac{2B}{3h}\sum_{n'(n'\neq n)}\left\{\frac{|M(n\,;\,n')|^2}{\nu(n\,;\,n')}\sum_{j,m}e^{-W(nj)/kT}\right\} \tag{16}$$

[29] Born, Heisenberg, and Jordan, Zeits. f. Physik, **35**, 605 (1926).

[30] P.A.M. Dirac, Proc. Roy. Soc. **111A**, 281 (1926).

[31] Born, Heisenberg, and Jordan deduce the formulas proposed by Goudsmit and Kronig and by Hönl for the relative intensities of Zeeman components. Dirac gives the rather more difficult derivation of the formulas advanced by Kronig, Russell, Sommerfeld and Hönl for intensities in multiplets. These various formulas are more comprehensive than but necessarily include the corresponding sum-rules for Zeeman and multiplet components.

[32] The ordinary statement of the sum-rule for the inner quantum number is essentially that the sum

$$\sum_{mj'm'}|M(njm\,;\,n'j'm')|^2 \tag{A}$$

is proportional to the a-priori probability p_j (cf. [27]) of the state j, assuming momentarily that j corresponds to the inner quantum number. Eq. (A) contains sums over m and m' inasmuch as the Zeeman components are supposed unresolved in the ordinary multiplet rule. The sum-rule for the magnetic quantum number shows that all the components of the state j contribute equally in the sum over m in (A). As there are p_j such components, the factor p_j thus cancels out if we do not sum over m in (A), thus making (15) invariant of both j and m.

The double sum in this equation is the same as the denominator of (6) inasmuch as on p. 736 we made the approximation $W(njm) = W(nj)$. Thus (16) becomes an expression

$$N\alpha = -\frac{2N}{3h} \sum_{n'(n' \neq n)} \frac{|M(n\,;n')|^2}{\nu(n\,;n')} \tag{17}$$

which is independent of T. This is the desired result, and (17) constitutes the "constant" part $N\alpha$ of the Langevin-Debye formula. The right-hand side of (17) does not involve the index m, or the direction of the axis of quantization,[33] and so the choice of this axis cannot influence $N\alpha$. It is clear that $N\alpha$ is positive since the $\nu(n;\, n')$ are negative or "absorption" frequencies.

Combination of the simplifications affected in the high and low frequency parts yields the complete Langevin-Debye formula $\chi = N\alpha + (N\mu^2/3kT)$.

Special case that F is the only external field. It is to be noted that the proof has nowhere assumed that the axis of spacial quantization is the same as the axis of the applied field F. Ordinarily, however, F is considered to be the only external field, and then these two axes will coincide. When this is the case there will be no external influences when $F=0$, and hence there will be no secular precessions about the axis of quantization before application of F. This means that the third index will have no influence on the energy in the absence of F and consequently that all frequencies of the form $\nu(njm;\, njm')$ will vanish, as the absence of the superscript $^{(F)}$ (cf. p. 734) means the frequencies are to be measured with $F=0$. Nevertheless there will be no trouble with zero denominators in Eqs. (3), (5), (7), (8), as the matrices $\boldsymbol{M}_z$ or $\boldsymbol{\mu}_z$ will contain no elements in which $m' \neq m$ since the z-component clearly cannot involve the frequency of precession about the z-axis, which is the direction of F. Thus in Eqs. (3), (5), (7), (11) the summation over m' may be replaced by the substitution $m' = m$.

4. The Fundamental Spectroscopic Stability Relation.

We have already mentioned that the high spectroscopic stability characteristic of the new quantum mechanics is the cardinal principle underlying the continued validity of the Langevin-Debye formula. We shall not attempt a precise definition of the term "spectroscopic stability."[34] It means roughly that the effect of orientation or of degeneracy in general is no greater than in the classical theory, and this usually implies that summing over a discrete succession of quantum-allowed orientations gives the same result as a classical average over a continuous distribution. In calculations of susceptibilities, and also in many other problems, the principle of spectroscopic

[33] It is obvious from the mode of definition that $M(n;n')$ cannot depend on the direction of the axis of quantization. Otherwise the total intensity of a spectral line, i.e., the x, y, and z effects combined, would depend on the direction of this axis, which is absurd.

[34] For references on spectroscopic stability and some discussion of its important application to the polarization of resonance radiation see J. H. Van Vleck, "Quantum Principles and Line Spectra," Bull. Nat. Research Council, no. 54, p. 171 ff.

stability may be regarded as embodied mathematically in the statement that the double sum

$$\sum_{l,l'} \left| f(sl\,;\, s'l') \right|^2 \tag{18}$$

is uniquely determined even in a degenerate system, and has a value invariant of the manner in which the degenerate degrees of freedom are quantized. Here $f(sl; s'l')$ denotes an amplitude element of any "quantentheoretische Grösse," i.e., of any matrix $\boldsymbol{f}$ which can be regarded as a function of the coordinates and momenta. We suppose the indices l and l' to correspond to a quantum number l whose value has no influence on the energy, while s and s' represent the effect of all other quantum numbers. The summation with respect to l extends over all the components of a family of states s whose energies ("Eigenwerte") coincide due to degeneracy. The interpretation of the sum over l' is similar. Thus the summation embraces all the various transitions which are possible between two "multiple" energy levels each composed of a number of equal-valued components. A simple physical illustration is summing over all the Zeeman components of a given spectral line in a vanishingly small magnetic field. The invariance of an expression similar to (18) has already been established by Born, Heisenberg, and Jordan[35] for the special case that only one of the systems of energy levels is multiple. This simplification would require that l (or else l') assume only one value in (18). The invariance of the more general expression (18) was mentioned without proof in a preceding paper by the writer,[36] and he is informed that the more general result has also been obtained independently by Born (unpublished). In the work of Born, Heisenberg, and Jordan, and of Born, it is supposed that $\boldsymbol{f}$ is a coordinate or momentum matrix, but this appears to be a needless specialization.

Proof. The demonstration is very similar to that given by Born, Heisenberg, and Jordan for the special case that one of the systems of levels s or s' is single, and we assume the reader has at least a superficial familiarity with their procedure[37] for quantizing the perturbations of a degenerate system. Let $\boldsymbol{S}$ be the "transformation matrix" associated with the passage from one mode of quantization of the degenerate system to another. The function $\boldsymbol{S}$ will generate a contact transformation from the original variables $\boldsymbol{p}_1^0, \cdots, \boldsymbol{p}_n^0, \boldsymbol{q}_1^0, \cdots, \boldsymbol{q}_n^0$ to a set of new variables $\boldsymbol{p}_1, \cdots, \boldsymbol{p}_n, \boldsymbol{q}_1, \cdots, \boldsymbol{q}_n$ by means of the connecting relations

$$\boldsymbol{p}_k = \boldsymbol{S}\boldsymbol{p}_k^0\boldsymbol{S}^{-1}, \quad \boldsymbol{q}_k = \boldsymbol{S}\boldsymbol{q}_k^0\boldsymbol{S}^{-1}.$$

If the system is made non-degenerate by applying an external field, the secular perturbations are calculated and quantized by finding the particular contact transformation which will reduce the perturbed energy to a diagonal matrix, but this fact is of no immediate consequence. Born, Heisenberg, and Jordan show[38] that in general

[35] Born, Heisenberg, and Jordan, Zeits. f. Physik, **35**, 590 (1926).
[36] J. H. Van Vleck, Proc. Nat. Acad., **12**, 662 (1926).
[37] Born, Heisenberg, and Jordan, Zeits. f. Physik, **35**, 577–590 (1926).
[38] Ibid., p. 574.

$$\boldsymbol{f}=\boldsymbol{S}\boldsymbol{f}^0\boldsymbol{S}^{-1} \tag{19}$$

where $\boldsymbol{f}^0$ is the same function of the $\boldsymbol{p}^0$'s and $\boldsymbol{q}^0$'s that $\boldsymbol{f}$ is of the $\boldsymbol{p}$'s and $\boldsymbol{q}$'s, so that

$$\boldsymbol{f}=\boldsymbol{f}(\boldsymbol{p}_1, \cdots, \boldsymbol{p}_n\,;\, \boldsymbol{q}_1, \cdots, \boldsymbol{q}_n) \qquad \boldsymbol{f}^0=\boldsymbol{f}(\boldsymbol{p}_1{}^0, \cdots, \boldsymbol{p}^0{}_n, \boldsymbol{q}_1{}^0, \cdots, \boldsymbol{q}_n{}^0).$$

Now we suppose $\boldsymbol{S}$ to be a "secular" transformation matrix associated only with the ambiguity arising from the degeneracy, and hence $S(sl\,;\, s'l')$ will vanish unless $s=s'$. This means simply that in the language of section 3, $\boldsymbol{S}$ possesses no "high frequency elements," and in, fact contains only elements associated with zero frequencies representing transitions between component states of coincident energy. Therefore by the rules for matrix multiplication an element of (19) may be written

$$f(sl\,;\, s'l')=\sum_{l'',l'''}S(sl\,;\, sl'')f^0(sl''\,;\, s'l''')S^*(s'l'\,;\, s'l'''). \tag{20}$$

Here we have made use of the fact[39] that in virtue of the orthogonality properties $\boldsymbol{S}^{-1}$ equals $\tilde{\boldsymbol{S}}^*$, where $\boldsymbol{S}^*$ denotes the conjugate of $\boldsymbol{S}$, and $\tilde{\boldsymbol{S}}$ the transposed matrix formed from $\boldsymbol{S}$ by interchanging rows and columns, so that $\tilde{S}^*(s'l'\,;\, s'l''')=S^*(s'l'''\,;\, s'l')$.

From (20) it is seen that

$$\begin{aligned}\sum_{l,l'}f(sl\,;\, s'l')f^*(sl\,;\, s'l')=\sum_{l,l',l'',l''',l^{\mathrm{iv}},l^{\mathrm{v}}}\{&f^0(sl''\,;\, s'l''')f^{0*}(sl^{\mathrm{iv}}\,;\, s'l^{\mathrm{v}})\\ &S(sl\,;\, sl'')S^*(sl\,;\, sl^{\mathrm{iv}})S^*(s'l',\ s'l''')S(s'l'\,;\, s'l^{\mathrm{v}})\}\end{aligned} \tag{21}$$

where we write l^{iv} for l'''', etc. Now the orthogonality relations[39] give

$$\sum_l S(sl\,;\, sl'')S^*(sl\,;\, sl^{\mathrm{iv}})=\delta(l'',\ l^{\mathrm{iv}}) \tag{22}$$

where

$$\delta(l'',\ l'')=1, \qquad \delta(l'',\ l^{\mathrm{iv}})=0, \qquad l''\neq l^{\mathrm{iv}} \tag{23}$$

There are also, of course, equations similar to (22) and (23) in which s, l, l'', l^{iv} are replaced by $s', l', l^{\mathrm{v}}, l'''$ respectively. Thus (21) becomes

$$\sum_{l,l'}f(sl\,;\, s'l')f^*(sl,s'l')=\sum_{l'',l'''}f^0(sl''\,;\, s'l''')f^{0*}(sl''\,;\, s'l'''). \tag{24}$$

Now on the right-hand side we may replace l'', l''' by l, l' for this is only a change in the notation for the variable of summation. Also the product of a complex number and its conjugate equals the square of its absolute magnitude. Therefore (24) may be written

$$\sum_{l,l'}\left|\, f(sl\,;\, s'l')\,\right|^2=\sum_{l,l'}\left|\, f^0(sl\,;\, s'l')\,\right|^2. \tag{25}$$

This is the desired result, for it shows that an expression of the form (18) has the same value before and after the transformation, and is thus invariant of the mode of quantization.

It is noted that the expression (18) is invariant even when $s=s'$, for there is nothing in the above demonstration which requires $s\neq s'$. With $s=s'$ the summation in (18) or (25) extends over the various transitions within a multiple level rather than over those between two multiple levels.

[39] Ibid., p. 584, Eq. (11).

Application to spacial degeneracy. The most important application of (18) or (25) in calculating susceptibilities is to the case where the degeneracy arises from the absence of an external field, so that one direction in space is as good as another. Then the various values of the indices l and l' correspond to different values of the axial (often called "equatorial" or "magnetic") quantum number belonging to a system of "multiple" levels whose components differ from each other only in that they represent different "quantum-allowed" orientations relative to the axis of quantization. The contact transformation of the type considered above then simply involves a rotation of the coordinate axes, and means that the direction of spacial quantization is shifted from one direction in space to another. Now clearly if $\boldsymbol{A}$ is any vector, the double sum (18) has by symmetry the same value whether we take $\boldsymbol{f}$ equal to any one of the three components $\boldsymbol{A}_x$, $\boldsymbol{A}_y$, $\boldsymbol{A}_z$ provided we average (18) over all possible directions for the axis of quantization, for after the average there is no preference between the x, y, and z directions without external fields. But we have proved an expression of the form (18) invariant of the axis of quantization, and hence the average over all directions for this axis is unnecessary. Thus (18) always has the same values with $\boldsymbol{f}$ equal to $\boldsymbol{A}_x$, $\boldsymbol{A}_y$, or $\boldsymbol{A}_z$ regardless of the choice of the axis of quantization. Hence, since $\boldsymbol{A}^2=\boldsymbol{A}_x^2+\boldsymbol{A}_y^2+\boldsymbol{A}_z^2$, it follows that

$$\sum_{l,l'} \left| A_x(sl\ ;\ s'l') \right|^2 = \tfrac{1}{3} \sum_{l,l'} \left| A(sl\ ;\ s'l') \right|^2 \tag{26}$$

with analogous equations involving A_y and A_z. This is the same result as was quoted on p. 737, section 3, except for a slight difference in notation. We there used the three-index notation $A(njm;\ n'j'm')$ instead of $A(sl;\ s'l')$ in order to permit further classification of the families of energy levels. The two indices n and j together correspond to s, and m to l.

The proof given above assumes complete spacial degeneracy, which means that the molecule should be subject to no external forces, and in section 3 we applied (26) to the "unperturbed motion" executed when the applied electric field F is zero. In section 3, however, we admitted the possibility of other simultaneous external fields independent of F (e.g., a "crossed" magnetic field), so that there was not necessarily spacial degeneracy and freedom from external influence when $F=0$. We can, nevertheless, still apply (26) to such cases if the result of these other external fields is only to introduce precessions or secular motions corresponding to frequencies of the form $\nu(sl;\ sl')$, without any "high frequency perturbations" of the type $(sl;\ s'l')$, $s'\neq s$. For then the effect of these external fields is given by a "secular" contact transformation of the type considered above, which will leave invariant the values of expressions similar to the left-hand side of (26). Actually an external field will in general alter to some extent the amplitudes of terms of the type $(sl;\ s'l')$ $(s'\neq s)$, but these "non-secular" perturbations will in general distort the amplitudes only to a low degree, as this is a well-known result in dynamics. Hence it is a good approximation to apply (26) even when the unperturbed motion corresponding to $F=0$ is itself a motion in some other external field. The usual case, of course, is

where F is the only external field, and then (26) holds rigorously for the unperturbed motion.

Illustrations of (26). An example or two will perhaps make the results obtained above more concrete. If $\mathbf{A}$ be a unit vector matrix, then $\mathbf{A}_x$ may be regarded as the cosine of the angle between this vector and some fixed direction in space chosen as the x-axis. Eq. (26) shows that the mean value of the square of the cosine of this angle is one-third when we average over all the various allowed orientations relative to the axis of quantization (not necessarily the x-direction). This is the same value as results by symmetry in the classical theory when we average over a uniform continuous distribution of orientations. This agreement is the underlying reason why the susceptibility formula (1) contains the factor $\frac{1}{3}$ quite as generally in the new quantum mechanics as in the classical theory.

Another simple illustration of (26) is furnished by the theory of diamagnetism. It can be shown that the diamagnetic susceptibility is proportional to x^2+y^2 if the magnetic field is applied in the z-direction. Now by the rules for matrix multiplication the average value of x^2 for the state s is

$$\sum_{l,s',l'} |\, x(sl\,;\, s'l')|^2/p_s \qquad (27)$$

where s' is to be summed over all possible states, including $s'=s$, and where p_s is the number of l-components belonging to the multiple state s. In other words p_s is the a-priori probability of the state s, or, what is essentially the same thing, the number of values assumed by its axial quantum number. Now (27) is simply an expression of the form (18) summed over s', and there are, of course, similar expressions for the y and z components. Hence by (26) the average values of x^2, y^2, and z^2 are equal, and since $r^2=x^2+y^2+z^2$, we can take $x^2+y^2=\frac{2}{3}r^2$, just as in the classical theory. This has an important experimental application, as it shows that the diamagnetic susceptibility per molecule should not vary with pressure (see ref.[36])

Department of Physics,
University of Minnesota,
February 28, 1927.

BOOK REVIEWS

Die Verwendung der Röntgenstrahlen in Chemie und Technik. HERMAN MARK. (Bd. XIV des Handbuch der angewandten und physikalischen Chemie herausgegeben von G. BREDIG.)—The author of this installment of one of the current hand-books has himself contributed much to the application of x-rays in research. The task which he sets himself is to present in one volume everything that the user of x-rays for other than medical purposes needs to know. He has come so near to complete success that his treatise deserves very careful consideration.

The first section (101 pages) deals with the production of x-rays. It contains rather too long and too elementary an account of the electrical engineering problems which may arise, and too much space is devoted to obsolete devices. On the other hand, the practical notes on the construction and use of gas-discharge tubes and electron-discharge tubes with demountable parts will probably save the novice—who is frequently in the author's thoughts—a good deal more than the cost of the whole volume. The American reader, however, will not give quite as much weight as his German contemporary to arguments against ready-made (technische) tubes, and other rather high-priced pieces of apparatus, partly because the cost of the experimenter's time is relatively more important here than in Germany.

The second section (104 pages) deals with the properties of x-rays. A good deal of this section is obvious padding. Flagrant examples are found in the tables of ν/R and $(\nu/R)^{1/2}$ and in Table 28, which gives data on K and L absorption edges for the light elements. Incidentally, the value of R given (pp. 128 and 447) is not the value (109737 cm^{-1}) used in the tables. Figs. 136 and 141 are meaningless as printed without any clue as to the abscissae. Tables 32, 37b and 38 have suffered similarly by amputation of footnotes. There are a good many misprints and many of the values quoted correctly are now obsolete. The Spectroscopy of X-Rays, by Manne Siegbahn, Oxford Univ. Press (1925), and the recent review by A. E. Lindh, Phys. ZS. **28** 24–62, 93–125 (1927), should be consulted in preference.

The third section (232 pages) is very much the best. The subject matter here is crystal structure and its analysis. The description of crystals, lattices and space-groups is based on books by Niggli and Wyckoff and is both full and clear. In Tables 52 and 52a (42 pp.), which belong in this section though printed as an appendix, an effort has been made to give by single entry all that can be written down concerning the symmetry and the coordinates of equivalent points in the 230 possible space-groups. This has required, among other things, a copying of Wyckoff's tables of coordinates. The success achieved in this monumental labor is only fair. No complete checking has been attempted but in about two-thirds of Table 52 and the associated part of Table 52a more than thirty errors have been found, any one of which might seriously delay an uncritical user. The coordinates (Table 52a) are so crowded together that the chance for mistakes in reading is considerable; space wasted in Table 52—"Koordinantenanfangspunkt" appears at full length more than a hundred times—would here have been appreciated. The advantage of single entry is partly counterbalanced by the necessity of consulting non-adjacent pages. Table 46 is inconsistent with Table 52 from which it should be derivable. In spite of the faults noted the tables in this section will find frequent use.

In the analysis of crystal structure by x-ray methods the various procedures are well explained and their advantages and draw-backs are fairly put. Examples of each are presented in such detail that a beginner in the art will find most of his questions anticipated and can proceed to actual anaylses with confidence. Such thoroughness as the author insists upon, involving in most cases the use of several different methods, would save the scientific public from many largely speculative "determinations" of crystal structure. The discussion of intensity in interference patterns of all sorts is especially good.

In the fourth section (12 pages) the reader meets with disappointment. Here the questions dealt with concern the sizes and orientations of the crystals in polycrystalline aggregates, in-

cluding colloids. The author has had so much to do with the second of the questions in researches on plastically deformed metals that one looks with confidence for a masterly account of the rather special artifices here necesssry. He finds instead only a few generalities and the excuse that the book is already too long to permit the inclusion of more. As already hinted, the earlier sections might better have been slashed to make room here. Radiography is even more completely crowded out.

A series of notes and references (27 pages) and a subject index (10 pages) complete the treatise. The references are adequate but not very carefully checked, especially as to the spelling of proper names. The illustrations throughout the book are generally good but often differ enough from the text to make it clear that the cuts were not all available for comparison when proof was read. The scale of reproduction is erratic, some unimportant sketches (e.g. Fig. 81) being too large—one is put in twice!—and some important ones (e.g. Fig. 74), too small. There is, in Section I, a tendency to use trade catalog cuts and patent drawings which are not very informative. Some figures contain absurd mistakes (e.g. Figs. 134 and 252). The paper is of good quality, the type is rather too thin and too much crowded together to make for easy reading. Large octavo. Pp. xiii+528, 328 figs. J. A. Barth, Leipzig. Price, cloth bd. Rm 50.00 ($12.00). L. W. McKEEHAN

Applied X-rays. GEORGE L. CLARK.—This book professes to be propaganda in favor of a wider use of x-rays, and as such it is excellent. It contains at least a brief mention of every known application, and enough detail in regard to every application not exclusively medical so that the reader can decide for himself whether x-rays are likely to be of service in any given case. No one responsible for improvements in an industry dealing largely with solid or semi-solid materials can fail, while reading it, to be impressed with the opportunities which x-ray methods offer him in the way of analysis, inspection and control. The style, which is emphatic, and the choice for detailed discussion of matters with which the author is personally familiar, conform well to the purpose intended. The mathematical knowledge required of the reader is not greater than can properly be expected, but sections here and there will prove difficult to one not familiar with the nomenclature of organic chemistry. Just these parts will most richly repay study by physicists. The long chapter on colloidal and amorphous structure in particular, describes experimental studies which are hardly, if at all, known to those whose interest in x-rays has been based on physics. There are, in this chapter and elsewhere, brief references to the author's own unfinished investigations and to finished work concerning which publication has until now been withheld. These notes and some practical advice in regard to experimental details make the book a primary as well as a secondary source of information which must be consulted by investigators.

There is urgent need for haste in the preparation of a book on x-rays, parts of which are sure to be out of date before they are printed. This explains, but does not excuse, the principal faults of the present volume. Of these the worst are carelessly worded statements, ambiguous or contrary to fact. For example, Kirchner's results on nickel steel are just the opposite of those credited to him (p. 172). Several errors creep in where the avoidance of explicit mathematics has forced the use of circumlocutions. References to periodical literature are too often defective in regard to volume number, page number or year of publication. Typical crystal structures (esp. pp. 145–6) have suffered from mistakes in copying or typesetting.

The author states (p. 175) that the diffraction rings characteristic of liquids are explicable only by transient lattice-structures or equivalent regularities in the arrangement of molecules. It has, however, been proven several times—most lately by F. Zernike and J. A. Prins, ZS. f. Phys. **41** 184–194 (1927)—that the mere existence in a liquid of a lower limit to the distance between molecule-centers is enough to explain the observed effects.

The paper, type, illustrations, index and binding are good. Large octavo. Pp. xiii+255, 99 figs. McGraw-Hill Book Company, New York City, Price $4.00. L. W. McKEEHAN

Practical Colloid Chemistry. WOLFGANG OSTWALD with P. WOLSKI AND A. KUHN. Translated by I. NEWTON KUGLEMASS and THEODORE K. CLEVELAND.—This book is a translation of the fourth edition of Dr. Ostwald's laboratory manual for students of colloid

chemistry. It is divided into ten chapters each one of which deals with an important phase of the subject. The ten chapters are entitled: I. Preparation of Colloidal Solutions; II. Diffusion, Dialysis, Ultrafiltration; III. Surface Tension and Viscosity; IV. Optical Properties; V. Electrical Properties; VI. Experiments with Gels; VII. Adsorption; VIII. Coagulation, Peptization and Related Phenomena; IX. Commercial Colloids and Other Material for Demonstration Purposes; X. Dispersoid Analysis. One hundred and eighty three experiments are listed in the first eight chapters. As these chapter headings indicate the student, performing these experiments, proceeds from a study of the methods for the preparation of colloids to their purification and then to a study of their properties. Each chapter begins with an explanation of the phenomena to be studied. The experiments themselves are for the most part very well chosen. In some instances however the directions are rather brief and not sufficiently specific. The translators should have used a little more care as there are some grammatical errors and the construction of some of the sentences is rather Teutonic. The book should be of considerable value as a laboratory guide to students entering the field of colloid chemistry. Pp. xvi+191. 22 figs. E. P. Dutton & Co. Price $2.25. L. H. REYERSON

Investigations on the Theory of the Brownian Movement. ALBERT EINSTEIN. Edited with notes by R. FÜRTH. Translated by A. D. COWPER. This volume contains five of the principal papers contributed by Einstein on the theory of the Brownian movement to the Annalen der Physik and the Zeitschrift für Elektrochemie during the period 1905 to 1911. The author has developed from first principles a mathematical theory of the movement and osmotic pressure of small suspended particles in a liquid and of their influence on the viscosity, etc., of the liquid, leading up to a determination of molecular dimensions. In the fifth paper is given a brief but comprehensive elementary theory of the Brownian movement. An appendix of notes by Dr. Fürth with corrections, later references, and some expansions of the original texts, is added. The work will serve as an admirable introduction to the study of osmotic pressure. The difficult task of the translator has not been particularly well done. The involved sentence structure of the original texts is often retained and makes anything but smooth reading. The typography, while adequate, is not distinguished, particularly in the mathematical forms. Pp. vii+124, 4 figs. E. P. Dutton, 1927. Price $1.75.

JOHN T. TATE

Treatise on Thermodynamics. MAX PLANCK. Translated by ALEXANDER OGG.—This is the third English edition, a translation of the seventh German edition, of Planck's classic. Its appearance is particularly welcome because the previous English editions have been out of date for twenty years or more. The principal addition to be found in the present volume is, of course, the chapter on the Nernst heat theorem. There is also included a discussion of Ghosh's theory of the lowering of the freezing point of strong electrolytes and of Debye's equation of state for solids which contains the explanation of the variation of the specific heat with temperature as well as Grüneisen's law for the coefficient of thermal expansion. It is unfortunate that Debye and Hückel's theory of electrolytic dissociation could not have been included. The numerical data have been thoroughly revised and brought up to date. Commendation is due the translator for the faithfulness and skill with which he has done his work. The book is attractively printed and serviceably bound. Pp. iv+297, 5 figs. Longmans Green and Co., 1927. Price $5.00.

JOHN T. TATE

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE LOS ANGELES MEETING, MARCH 5, 1927.

The 144th meeting of the American Physical Society was held in Los Angeles, California, at Berkeley Hall, University of California at Los Angeles.

The presiding officer was Professor S. J. Barnett. The attendance was about 40.

The program consisted of 31 papers, of which abstracts are given in the following pages. An **AUTHOR INDEX** will be found at the end.

D. L. WEBSTER,
Local Secretary for the Pacific Coast

ABSTRACTS

1. The reflection of x-rays by crystals as a problem in the reflection of radiation by parallel planes. SAMUEL K. ALLISON, University of California.—It is pointed out that the previous solutions of the problem of the reflection of radiation by parallel planes by Lamson and Gronwall are physically incorrect since the intensities, not the amplitudes, of contributions from individual planes, have been added. It is shown that a mathematical method due to Darwin leads to a solution identical mathematically with those of Lamson and Gronwall. Using this result, the intensity of reflection is evaluated for certain ranges of the constants directly related to the reflected and transmitted amplitudes due to a single plane.

2. A study of the infra-red solar spectrum with the interferometer. HAROLD D. BABCOCK, Mount Wilson Observatory.—*Solar wave-lengths in the infra-red.*—The solar spectrum in the interval λ6869–8980 has been photographed on plates sensitized with *neocyanine* through interferometers crossed with a concave grating. Of the 507 *lines measured*, 176 are of solar origin; most of the remainder are probably lines of terrestrial water vapor. The *wave-lengths* were measured in terms of oxygen band lines due to terrestrial absorption and are expressed on the *neon scale. Identification of solar lines.*—The measurements have been used for a revision of the identification of solar lines, but refined laboratory wave-lengths are much needed for further work. The more prominent solar lines still awaiting identification are listed. *Differences between solar and terrestrial wave-lengths.*—In the absence of precise laboratory data for vacuum spectra in the infra-red, the new solar wave-lengths are compared with interferometer measurements on the spectrum of a short iron arc at atmospheric pressure. This brings out clearly the correlation of multiplet grouping, excitation potential and behavior under increased excitation with the combined influence of pressure displacement and pole effect. The data, though not definitive, are consistent with the gravitational displacement predicted by Einstein.

3. Fine structure of the Balmer lines of hydrogen. NORTON A. KENT, LUCIEN B. TAYLOR and HAZEL PEARSON, Boston University.—Using two optical trains (1) two crossed Lummer plates, the larger of resolving power 670,000, and (2) an echelon of resolving power 660,000, with a vacuum tube cooled with liquid air, the writers have determined the wave-length difference between the two well known components, λ' and λ'' ($\lambda' > \lambda''$) of Hα, Hβ and Hγ.

The doublet separations are shown in the table together with those given by Houston, which latter are in our estimation, the most reliable thus far obtained.

	Houston	Kent, Taylor and Pearson	
Current density	250	25	13 ma./sq. cm
$\Delta\lambda$ for Hα	0.1358	0.1370	0.1391 Angstroms
$\Delta\lambda$ for Hβ	.0782	.0791	———
$\Delta\lambda$ for Hγ	.0665	.0666	———

Our values are higher but this is not to be wondered at, because of the different current densities employed. A very reliable Lummer plate spectrogram, taken at 13 milliamperes per sq. cm, yields 0.1391 for Hα, which is in harmony with such a current change. Microphotometer curves of *enlargements* of the original Lummer plate negatives reveal another component in λ', unresolved but unquestionably present, in Hα, Hβ and Hγ. Hansen noticed assymmetries here in Hα and Hβ. Further these are indications of another component in λ''. The *magnitudes* of these six new components all agree well with the theoretical magnitudes on the spinning electron theory: their *positions* are in all cases too far toward the red—an effect probably due to the photographic processes involved.

4. The fine structure of the helium arc spectrum. WILLIAM V. HOUSTON, National Research Fellow, California Institute of Technology.—By means of the compound Fabry-Perot interferometer it has been possible to show that both the sharp series line 7065 and the diffuse series line 5876 of the orthohelium spectrum are triple. Under conditions which made reversal very improbable the strong component was shown to consist of two lines with intensity ratio about 5:3. This, with the weak component, makes a triplet of normal intensity ratios, and confirms the theoretical expectation that the helium spectrum should consist of singlets and triplets. The 2^3P level is inverted with separations 0.992 cm^{-1} and 0.071 cm^{-1}. This is in good agreement with the quantitative theory of Heisenberg. The D levels can be estimated from the 5876 line to be partly inverted. This experimental verification of the theoretical expectation removes the helium spectrum from its anomalous position among the spectra of the elements.

5. Series spectra of ionized phosphorus, P$_{II}$. I. S. BOWEN, California Institute of Technology.—One hundred and ten of the strong lines of P$_{II}$ have been classified as arising from various combinations between thirty-two terms of the triplet system. The observed terms include nearly all the terms of the triplet system that are predicted by the Russell-Heisenberg-Pauli-Hund theory for the s^2p^2, sp^3, $s^2p\cdot 4s$, $s^2p\cdot 5s$, $s^2p\cdot 4p$, $s^2p\cdot 3d$, and $s^2p\cdot 4d$ configurations. The lowest level is the $^3P_0$ term of the s^2p^2 configuration. This term has a value corresponding to an ionization potential of 19.82 volts.

6. Relationships in the spectra of the elements of the first row of the periodic table. R. A. MILLIKAN and I. S. BOWEN, California Institute of Technology.—Practically all of the strong ultra-violet lines that can be emitted by the atoms of the first row of the periodic table in all stages of ionization of the valence electrons have now been obtained and a general statement of the relationships between the frequencies of these lines has been formulated. These relationships are presented most simply and compactly in a new graph here given which depicts the generalized form of the Moseley law in the field of optics. Similarly a table of the ionization potentials of the atoms of the first row in all stages of ionization is here presented. Furthermore the predictions of the Russell-Heisenberg-Pauli-Hund theory as to the structure of spectra in general have been completely verified in the case of these light elements.

7. Interferometer Measurements on the Balmer Series. WILLIAM V. HOUSTON, National Research Fellow, California Institute of Technology.—The compound Fabry-Perot interferometer, with a resolving power of about one million, shows an unmistakable asymmetry of the short wave-length component of Hα. Graphical analysis of a microphotometer curve indicates the presence of a component about 0.12 cm^{-1} from the principal one, with about one sixth its

intensity. The presence of this component is the principal difference between the prediction of the spinning electron theory and that of the purely relativity theory. The observed intensity agrees well with that predicted by Sommerfeld and Unsöld. The intensity relations predicted by Sommerfeld and Unsöld make it possible to compute the position of each of the five components from the observed positions of the two centers of gravity. With the interferometer wave-lengths of the first three lines of the Balmer series R_H is found to be $109677.67 \pm .01$. Thus the accuracy of e/m, determined spectroscopically, is governed by the accuracy of R_{He}. From a mean of the values of Paschen and of Leo on He 4686, e/m is found to be 1.769, and it seems improbable that it can be below 1.765. This does not agree with the Zeeman effect measurements by Babcock, so that further work will be done with the interferometer to improve the value of R_{He}.

8. New infra-red absorption bands in methane. JOSEPH W. ELLIS, University of California, Southern Branch.—A recording infra-red spectrograph was employed to examine the absorption spectrum below 2.8μ of an 87.5 cm cell of pure methane. Five new absorption bands were found at 1.15μ, 1.37μ, [1.66μ, 1.72μ], and 1.80μ. Those at 1.66μ and 1.72μ are assumed to be the partially resolved first harmonic of the well-known fundamental at 3.33μ, while the 1.15μ maximum is interpreted as its unresolved second harmonic. The deviation from a true harmonic relationship is consistent with theory. The 1.37 and 1.80μ bands are doubtless the $(\nu_3'+\nu_4)$ and $(\nu_1+\nu_4)$ combination bands, where ν_3', ν_4 and ν_1 are the frequencies of the 1.69, 7.67 and 2.37μ bands respectively. The latter two values, as well as that at 3.33μ, are from measurements by Cooley (Astrophys. J., **62,** 73 (1925).), and the notation is consistent with his. The theoretical values of the above two combination bands are 1.38 and 1.80μ respectively. The degree of complexity recorded by Cooley in the 2.35μ region is also observed in this investigation. As a result of a check on the previous calibration of the instrument the wave-length values recorded in this abstract are slightly inconsistent with all values previously published by the writer. This correction will be more fully discussed elsewhere.

9. On King's classical theory of atomic structure. BORIS PODOLSKY, California Institute of Technology.—An analysis of King's paper (A Classical Theory of Atomic Structure and Radiation, Mercury Press, Montreal) shows that King assumes all electrons spinning with the same angular velocity. In motion the electron experiences a Lorentz-Fitzgerald contraction which is supposed to cause a precession. By assuming that the frequency of precession must equal the frequency of incident radiation in the case of photo-electric phenomena, and to an integral multiple of the orbital frequency in the case of radiation King obtains a picture of the quantum mechanism. There are, however, grave objections against this ingenious hypothesis. It is shown in the present paper that (a) the electron could not have a precession and absorb energy without changing the frequency of precession, (b) the electron cannot have a precession, (c) the picture is undesirable, for the precession of the electron (due to causes other than those discussed by King) has found its place in explaining the normal doublets and triplets, i. e. small changes of frequency and not the whole effect.

10. The magnetic dipole in Schroedinger's theory.—PAUL S. EPSTEIN.—Let us consider an electron moving in the field of a fixed nucleus to which a magnetic dipole of fixed direction is attached. It is known that in Bohr's theory this mechanism leads to the same energy levels as a spinning electron in the field of a simple nucleus, provided that we choose the moment of dipole as one half of the moment which a spinning electron would have. The calculations for this case have been carried out from the point of view of Schroedinger's undulatory mechanics and the final formulas are exactly those anticipated by Goudsmit and Uhlenbeck for the spinning electron.

11. Striking potentials of metallic arcs in vacuo. S. H. ANDERSON, University of Washington, —Simmon's theory of the minimum striking potential of metallic arcs in vacuo (Phil. Mag. **46.** pp. 816–819, 1923) has been tested with electrodes of magnesium and of aluminum. The electrodes were sealed into Pyrex glass bulbs (with one electrode adjustable by an electromagnet

outside) so that a high vacuum could be produced and maintained. With pressures of 10^{-4} bars, 1 bar and 10 bars, respectively, a persisting arc could *not* be struck with either kind of electrodes when potentials as high as 150 volts were applied. With a pressure of 100 bars of air, persisting arcs were struck with both the magnesium and aluminum electrodes. For magnesium the applied potential difference was 45 volts. While burning, the potential difference was 26 volts and the current 4 amperes. For aluminum the applied potential difference was 88 volts. While burning, the potential difference was 36 volts and current 3.1 amperes. It appears that the striking potential is dependent upon a gaseous atmosphere as well as the nature of the electrodes.

12. Mobilities of ions in hydrogen gas mixtures and the constitution of the ion. LEONARD B. LOEB, University of California.—Recent measurements of mobilities in HCl-air mixtures indicated that there was an increased concentration of HCl gas in the neighborhood of the ion, the effect being greatest for the negative ion. Experiments in mixtures of hydrogen with ether, and hydrogen with NH_3 have given the following new facts. Small amounts of ether *lower* the mobility of the *positive ion* in H_2 *abnormally* while the effect on the negative ion can be calculated from the law of mixtures. *Minute traces of* NH_3 in H_2 *increase* the mobility of the *positive ion to nearly that of the negative ion.* Further additions of NH_3 *lower* both positive and negative mobilities in H_2 faster than the law of mixtures demands, but not as fast as earlier experiments in air—NH_3 mixtures led one to believe. In a mixture of NH_3, ether, and H_2 the effect on the positive ions was to be calculated from the observed combined effects of what the ether alone produced added to what the NH_3 would have produced on a normal positive ion in H_2 without the increase due to NH_3 alone. These results can only be explained on the assumption that the ionized positive molecule or atom adds to itself at least one more molecule to make a positive ion. This conclusion is in accord with a similar conclusion recently drawn by Erikson on the basis of other evidence.

13. The effect of added gases on ammonia decomposition by optically excited mercury vapor. A. C. G. MITCHELL and R. G. DICKINSON, California Institute of Technology.—Ammonia decomposition has previously been shown to be sensitized to the mercury line 2537A by the presence of mercury vapor. In the present work the effect of added hydrogen, nitrogen, and argon on the rate of this decomposition has been studied, and the results correlated with the quenching of fluorescence of mercury vapor by these gases. It was found that with an ammonia pressure of 3 mm, a hydrogen pressure of about 0.1 mm suppressed the rate of decomposition by 50 percent; at lower ammonia pressures even less hydrogen was required. From the results of experiments at different ammonia and hydrogen pressures, the ratio of the efficiency of activation of ammonia by excited mercury, to the efficiency of de-activation of excited mercury by hydrogen has been estimated to be about 4×10^{-2}. On the other hand, several tenths of a millimeter of either argon or nitrogen were found to be without effect, as would be anticipated from the results of fluorescence experiments.

14. Direction of photo-electric emission. D. H. LOUGHRIDGE, California Institute of Technology.—Cloud expansion photographs of the photo-electrons produced in hydrogen, air, and argon by means of the $K\alpha$ radiation of Mo show that the most probable direction of emission is the same for all three gases, and forms an angle of about 70° with the x-ray beam. These angles have been measured by means of a stereoscopic comparator specially built for the purpose. The total number of tracks measured is 443. Distribution curves plotted with number of tracks starting at a given angle with the x-ray beam against the angle show a narrower peak for hydrogen than for the argon. This qualitatively supports the view that the distribution is due to secondary scattering by the electrons in the atoms through which the photo-electron passes and that the initial direction of emission may be constant for a definite wave-length and depend only on the radiation.

15. The velocity and number of the photo-electrons ejected by x-rays as a function of the angle of emission. E. C. WATSON, California Institute of Technology.—Magnetic spectra of the electrons ejected by x-rays from thin metallic films at angles ranging from 0° to 180° with

the direction of the x-ray beam have been obtained by the method of Robinson, de Broglie, and Whiddington. To the degree of accuracy of the measurements (0.5 percent) the maximum velocity of ejection is exactly the same in all directions. With thin foils of the heavier elements the numbers of electrons leaving the foil with this maximum velocity in the various directions is approximately the same. With foils of the very light elements, or with sputtered films so thin that Wentzel's criterion for single nuclear scattering holds, the number of electrons leaving the foil is greatest in a direction a little forward of perpendicular to the direction of the x-ray beam. The number of electrons leaving in other directions can be calculated by means of the theory of scattering, if the assumption is made that all the electrons start out from the atom in the same direction.

16. Spacial distribution of the photo-electrons ejected by x-rays. E. C. WATSON, California Institute of Technology.—The experiments of Wilson, Auger, Bothe, Bubb, Loughridge, and Kirchner have shown that the most probable direction of the photo-electron tracks in a gas traversed by x-rays is nearly the direction of the electric vector of the incident wave, but with an appreciable forward component. There is, however, a very considerable variation in the direction of the tracks. Theories to account for this apparent emission from the atom over a wide range of angles instead of in a definite direction have been proposed by Bothe, Bubb, Auger and Perrin, and Wentzel. It can be shown, however, that scattering must be present in all the experiments in sufficient amount to account for the distribution in direction, and the theory of scattering leads to a distribution function which fits the facts much better than any of the more elaborate theories. Consequently the fact that the photo-electron tracks do not have one definite direction does not constitute evidence for orbital velocities inside the atom.

17. The Shadowgraph Method as applied to a Study of the Electric Spark. HARVEY A. ZINSZER, Indiana University.—The method employed was essentially that devised by Foley and Souder (Phys. Rev. **25,** 373, 1912.) Instantaneous shadowgrams having an exposure of the order of three microseconds were obtained. Introducing low values of inductance between the influence machine and the retarding capacity showed an improvement in the method of controlling the retardation of the illuminating spark; a micrometer auxiliary gap located outside the dark box and in parallel with the object gap both permitted the photographing of very early sparks and considerably improved the detail of all shadowgrams whether of early or late sparks. The diffusion of metallic vapor into the spark gap as proved spectroscopically was verified by instantaneous photography. Photographic life histories of various types of spark discharges were obtained and a theory of the phenomena involved in the condensed electric spark discharge was subsequently proposed.

18. Some remarks on the formation of negative ions. A. P. ALEXEIEVSKY, University of California (introduced by L. B. Loeb).—When an electron approaches a molecule of a gas, the molecule is polarized and the electron is attracted toward the molecule. The force of attraction is probably given approximately by Langevin's expression $f=(D-1)e^2/2\pi r^5 N=K/r^5$ where D is the dielectric constant of the gas, N the number of molecules in 1 cc of gas, e the charge of the electron, and r the distance between the electron and the center of the molecule. An electron which has "attached" itself to a molecule is probably moving in an orbit a part of which lies inside the molecular core and the remainder outside it. Assuming that the electron cannot move inside the core all the time it is shown that all possible periodic orbits must lie inside a circle of radius $r=(Km)^{1/2}/p$ where m is the mass and p the angular momentum of the electron. Assuming that the least amount of angular momentum an electron can have is one Bohr unit it is found that for a given gas all periodic orbits must lie within the circle of radius $R=2\pi(Km)^{1/2}/h$ where h is Planck's constant. It turns out that for helium and argon R is less than the radius of the core, while in gases with large dielectric constant R is considerably greater than the probable radius of the core.

19. Factors influencing thermionic emission. A. KEITH BREWER (National Research Fellow), California Institute of Technology.—The thermionic emission from gold has been determined in the presence of various gases at atmospheric pressure. Both the positive and

negative currents follow the Richardson equation, although there is no semblance of saturation. A distinct proportionality exists between the difference in the values of b, (Δb), for the positive and for the negative emission, and for the corresponding differences in the values of T, (ΔT). Again, when an emitter, such as iron, is slowly oxidized over, there is a gradual increase in the values of b and T for the positive emission which is concomitant with a corresponding decrease for the negative emission. When the value of b is the same for ions of each sign T is likewise the same. The relationship between Δb and ΔT is accounted for by the presence of an intrinsic force, possessing the properties of a resultant field, existing at the surface. The changes in T and b accompanying the oxidation of a surface is doubtless due to the presence of the negative oxygen ions of the oxide neutralizing the positive intrinsic field, and upon high oxidation, actually giving rise to a resultant negative field.

20. Remark on the theory of the Trouton and Noble experiment. PAUL S. EPSTEIN.—The physical cause why this experiment must be negative in the theory of relativity can be stated as follows: the torque acting on the moving condenser is compensated by the fact that the longitudinal and transverse masses of the condenser are not equal but stand in the ratio $1-v^2/c^2$ (v velocity of the condenser, c of light). To obtain the components of the acceleration the longitudinal and transverse ponderomotive forces on each plate must be divided by the corresponding masses. The resultant acceleration passes through the center of gravity of the system and so does not produce any rotation. It is usually overlooked, that in the absolute theory also we must distinguish between longitudinal and transverse mass, since the nuclei have an electric constitution. For instance, if we imagine them as rigid electrified spheres the ratio is, according to Abraham's theory, $1-4v^2/5c^2$. In this case we still have a compensation of 4/5 of the torque and the effect is five times smaller than that expected under the assumption, usually made, that the whole of the torque can be observed. R. Tomaschek (Ann. d. Physik 78 p. 743, 1925) and C.T.Chase (Phys. Rev. 28, p. 378, 1926) give the maximum velocity that could remain undiscovered by them as 4 km/sec. Our remark would bring it to $4(5)^{1/2}$ km/sec $=9$ km/sec, so that their results are hardly fit to check Miller's contentions.

21. Measurement of wave-length in water. ARTHUR W. NYE, University of Southern California.—A transmission grating was submerged in a trough of water and mounted on the stage of a spectrometer in the usual position. A window behind the grating allowed parallel light to enter at right angles to the window and grating. The diffracted first and second order spectra were received by the telescope as usual, except that the front surface of the objective was in water. A watertight flexible rubber connection was provided so that the front of the objective could remain in water, but allow the telescope to be swung freely to observe the spectral lines. The usual equation then applied but the wave-lengths as calculated were the lengths in water. The inverse ratio of these to the accepted values in air should give the air-water index of refraction. The results showed that the index of refraction differed not more than 0.0025 from the accepted values, at any point. Several prominent lines of Hg and Na were used, ranging from about 4000A to 6500A.

22. End corrections of pipes as a function of frequency. FLOYD C. OSTENSON and S. H. ANDERSON, University of Washington.—The correction due to the reflection of sound waves from the open end of a brass pipe has been measured by the usual method of finding two or more resonant lengths. Points of resonance were located using as a detector a telephone connected to a galvanometer through a thermionic tube as a rectifier. With a tube 10 cm in diameter there is a small constant increase in the end correction with increasing frequencies from 128 v.p.s. to 832 v.p.s., beyond which the increase becomes very rapid. With a tube 7.62 cm in diameter there is a maximum in the end correction at 640 v.p.s. beyond which there is a decrease.

23. The measurement of sound-absorption in a room. V. O. KNUDSEN, University of California, Southern Branch.—The differential equation for the status of sound energy in a room yields two useful relations for determining a, the sound-absorption of a room. These

relations are (1), $a=4E/vI_{max}$, for steady state; and (2), $I=I_{max}e^{-avt}/4V$, for decay. (E= rate of emission of source, v=velocity of sound, I=average energy density, V=volume of room.) The usual method, developed by Sabine, makes use of (2), measuring the time t for a known diminution of intensity I. The advantages and limitations of this method, and also of two other possible methods, one involving the measurement of the average value of I_{max}, and another involving measurements of oscillograms of the decay of sound, are discussed. With suitable instruments, the measurement of I_{max} seems to be the most satisfactory method for determining a. Preliminary experiments and results are described which indicate that a, determined from (1) by intensity measurements, agrees within 2% of the value obtained from reverberation measurements. The frequency of the sound-source used varies periodically from 408 d.v. to 629 d.v. This shifts the interference pattern sufficiently to give approximately an average intensity of sound at any point in the room not too near the source.

24. Change of elastic frequencies in solid bodies with pressure. F. ZWICKY, California Institute of Technology.—The general theory for the constituent forces in heteropolar crystals has been developed by Born and other investigators. As a new conclusion of this theory a formula for the shift of frequency of residual rays with pressure is deduced. The shift corresponding to a pressure of 10,000 atm. amounts approximately to 7μ in the case of NaCl (residual rays at 50μ). Qualitative conclusions may be drawn with respect to the dependence of elastic frequencies on pressure in any crystal. Combining these results with a suggestion made first by Grueneisen, a rational explanation can be given for the effect of pressure on the specific electric conductivity of metals, this conductivity being in general increased with pressure. The relation of our results on conductivity to those obtained previously by Grueneisen and Bridgman in a quite different way, is discussed.

25. Effect of oil in storage on lightning discharge. ROYAL W. SORENSEN, California Institute of Technology.—As a part of a large laboratory program to determine means of protection against direct hits or induced sparks in oil reservoirs as produced by cloud charges or lightning strokes, a number of tests were made to determine the ability of oil to hold an electric charge or to influence the direction of discharge between electrodes on one of which oil is placed. These experiments show that as soon as oil is placed in an electric field circulation begins. Because of this oil does not act as a solid dielectric. That is, local charges cannot accumulate at spots on an oil surface. This point was proven by placing pans containing oil in a strong electric field produced by high-potential direct current. Charges could be detected on the surface of the oil only while the field was maintained between pan and an electrode above the oil. No charges were found after the source of energy was disconnected. Also, charged electroscopes when placed in contact with the surface of the oil will readily discharge. Other tests with the oil pan positive and the electrode above the pan negative also show that oil on a positive terminal does not influence spark discharge as does solid dielectrics placed near the positive terminal.

26. On the electrostatics of the thunderstorm. A. W. SIMON, California Institute of Technology.—The electrostatic phenomena of the thunderstorm are analyzed in somewhat greater detail than has been done before. The action of the storm cloud is shown to be analogous to the generation of charges and potentials by rubbing together two dissimilar substances, i. e., the fundamental experiment of frictional electricity. The generation of potentials and electric stresses by precipitation of charged rain and by the induction of charges at the earth's surface are discussed. It is shown that the "impulsive rush" lightning discharge of Lodge is electrostatically impossible. A relation between the change of gradient in an area, the polarity of the charged rain falling in the area, and the polarity of the overhead cloud is developed. Approximate numerical relations between gradients, charges, and potentials are deduced. Applications of the results to lightning protection are made.

27. Vacuum switch. H. E. MENDENHALL, California Institute of Technology.—Previous experiments on denuding metals of gases by various kinds of treatment have shown that arcing between contact points became continuously more and more difficult with further denudation, and suggested the possibility of interrupting large currents at high potentials in a

practically perfect vacuum without appreciable arcing. Experimental tests have now been carried up to the point where about 1000 amperes alternating current have been successfully interrupted at about 45,000 volts with practically no arcing. This report contains the details of these experiments.

28. Measuring the evaporation from a body of water. BURT and PAUL RICHARDSON. California Institute of Technology.—The method developed at this Institute by Cummings (Phys. Rev., **25**, 721, 1925; Jour. Electr., **46**, 491) and Bowen (Phys. Rev., **27**, 779, 1926) for measuring the evaporation from a body of water was employed under dissimilar circumstances in Pasadena and at Fort Collins, Colorado, to obtain results which show the relative importance of each factor in the evaporation equation of Cummings and Bowen: $I=S+LE(1+R)+U$, where I is the radiant energy integrated over any time interval, or more specifically, the solar and sky radiation in calories per sq. cm. corrected for reflection and back radiation. S is the heat energy represented by change in temperature of the water. LE is the latent heat represented by the evaporation during the same interval, L being the latent heat of evaporation, R represents the ratio of heat losses by convection and by evaporation, while U represents a relatively small correction for other losses.

29. Motion of an airship in a variable horizontal wind. H. BATEMAN, California Institute of Technology.—In the well known method of aerial navigation by dead reckoning the analysis is very simple when there is no wind or when the wind is uniform in velocity and direction. In the case of a variable wind the problem is complicated and so much is unknown that few results of importance can be expected. The problem is, however, mathematically interesting. Taking the case in which the wind blows in one direction and assuming that the propeller thrust depends linearly on the relative velocity, the problem reduces to a boundary problem for a certain type of linear differential equation of the second order. A solution of the problem is obtained for a case in which the wind drops steadily from one velocity to another.

30. A vertical seismometer. SINCLAIR SMITH, Mount Wilson Observatory.—An investigation of the properties of a flat spring when bent into a bow by two opposing collinear forces showed that over a limited range, the ratio of the total force to the force per unit extension becomes large. This property was made use of in the construction of a small vertical seismometer. Using a spring 12 cm long in a modified Galitzin form of instrument having a steady mass of 100 g. a period of 12 seconds was obtained. This instrument, however, differs from the Galitzin form in that it has a much larger range of stability and does not require such critical adjustments.

31. The Michelson-Gale earth-tide experiment repeated in Pasadena, California. W. T. WHITNEY, California Institute of Technology.—In this experiment, repeated in Pasadena under the direction of Dr. A. A. Michelson, a continuous record of the small tides in a north-south pipe and an east-west pipe, half filled with water, was obtained for the year 1924. A reduction of the observed pipe tides for the principal or semi-diurnal lunar tide, indicates clearly the loading due to the oceanic tides and a comparison of the relative phases of the pipe tides, the theoretical earth tide and the estimated phase of the ocean loading, indicates that the tilting in Pasadena due to the ocean load is approximately 2.5 times as great as that due to the earth tide proper. These results are obtained from a study of the north-south pipe tides only. The behavior of the east-west pipe tides seems anomalous and the controlling factors have not yet been isolated. It seems reasonable to suppose, however, that the local geologic configurations of fault planes and mountain blocks contributes in some manner to these irregularities. A small progressive tilt of this region is suspected though local conditions prevent a definite conclusion at this time.

AUTHOR INDEX

Alexeievsky, A. P.—No. 18
Allison, Samuel K.—No. 1
Anderson, S. H.—No. 11
———— see Ostenson
Babcock, Harold D.—No. 2
Bateman, H.—No. 29
Bowen, I. S.—No. 5
———— see Millikan
Brewer, A. Keith—No. 19
Dickinson, R. G.—see Mitchell
Ellis, Joseph W.—No. 8
Epstein, Paul S.—Nos. 10 and 20
Houston, William V.—Nos. 4 and 7
Kent, Norton A., Lucien B. Taylor and Hazel Pearson—No. 3
Knudsen, V. O.—No. 23
Loeb, Leonard B.—No. 12
Loughridge, D. H.—No. 14
Mendenhall, H. E.—No. 27
Millikan, R. A. and I. S. Bowen—No. 6
Mitchell, A. C. G. and R. G. Dickinson—No. 13
Nye, Arthur W.—No. 21
Ostenson, Floyd C. and S. H. Anderson—No. 22
Pearson, Hazel—see Kent
Podolsky, Boris—No. 9
Richardson, Burt and Paul—No. 28
Simon, A. W.—No. 26
Smith, Sinclair—No. 30
Sorensen, Royal W.—No. 25
Taylor, Lucien B.—see Kent
Watson, E. C.—Nos. 15 and 16
Whitney, W. T.—No. 31
Zinszer, Harvey A.—No. 17
Zwicky, F.—No. 24